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SIGNED: 

APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

J. O. L. WENDT
Associate Professor of Chemical Engineering
To Oscar and Lila, my Parents
AKNOWLEDGMENT

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ABSTRACT

The factors which influence the conversion of fuel nitrogen to nitrogen oxides during char combustion were examined as well as the role of diffusion and reaction both within the particle pore and outside the particle in a surrounding stagnant film.

It was found that at low temperatures, such as are applicable to fluid bed combustion, pore size is important and that high NO fluxes are favored by short wide pores.

The model developed provided significant insight into mechanisms of NO formation and predicted the observed weak temperature dependence of fuel nitrogen conversion. It also predicted a significant effect of particle size. It was found that the CO concentration in the free stream was likely to be a more important variable than the oxygen concentration in determining the overall effect of excess air.
CHAPTER 1

INTRODUCTION

The objective of this work was to determine theoretically the chemical and physical factors which affect nitrogen oxide formation during coal and coal char combustion and to analyze how particle characteristics such as porosity, particle size, and surrounding film thickness affect the conversion of fuel nitrogen to nitrogen oxides. The hope is that the theoretical insight so obtained will lead to air pollution abatement by combustion modifications.

Nitric oxide, NO, and nitrogen dioxide, NO₂, are among the principal air pollutants associated with combustion processes. Nitrogen dioxide is corrosive, toxic and a major participant in the formation of photochemical smog and thus a major cause of reduction in atmospheric visibility. Nitric oxide in the atmosphere is oxidized to NO₂ (Altshuller 1956, Leighton 1961).

There are two major sources of NOx emissions in the U.S.: stationary sources composed of power plants, industries, home and heating plants, and non-stationary sources composed of motor vehicles. In a report by the National Air Pollution Control Administration it was shown that in 1968, coal, oil, natural gas and gasoline combustion accounted for over eighteen out of an estimated twenty millions tons of man-made NOx in the United States. Of the ten million tons generated by stationary combustion sources, coal emitted four million
tons, fuel oil one million tons, natural gas 4.8 million and wood the remaining 0.2 million tons. An estimated eight million tons were emitted from non-stationary sources.

The proposed delay in auto NOx emission controls focuses increased attention on the problem of control of NOx emissions from stationary sources so that ambient NO2 standards can be met in the near future.

**Formation of NOx from Combustion**

There are two major mechanisms for the formation of NOx during combustion of coal, oil and natural gas. Most widely recognized is the mechanism involving the high temperature-thermal fixation of molecular nitrogen in the combustion of air. The nitrogen oxides produced by this mechanism are known as thermal NO (Pershing and Berkau 1972, Martin and Berkau 1972a,b) because the mechanism requires very high combustion temperatures to be effective. Pollutants in this case can be produced from essentially clean fuels such as natural gas or gasoline.

Another mechanism receiving increasing attention is that involving the reactions of atmospheric oxygen with nitrogen that is chemically bound in the fuel. The nitrogen oxides produced by this mechanism are known as fuel NOx and do not require high combustion temperatures (Pershing and Berkau 1972, Martin and Berkau 1972a,b, Bartok, Crawford and Piegari 1972, Wendt, Sternling and Matovich 1972, Sternling and Wendt 1972, Thompson, Brown and Beer 1972). Both
mechanisms will result primarily in NO rather than NO₂ because the residence time in most stationary combustion processes is too short for the oxidation of NO to NO₂.

The principal reactions in the high temperature fixation of atmospheric nitrogen (thermal NO) are generally agreed to be those proposed by Zeldovich (1946).

\[ \text{N}_2 + \text{O} \rightarrow \text{NO} + \text{N} \quad (1) \]

\[ \text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O} \quad (2) \]

Reaction 1 has a high activation energy (74 Kcal) and is rate controlling. This strong temperature dependence results from breaking the strong N≡N bond and is the key to many effective NOₓ abatement methods which involve a reduction in peak flame temperature.

The formation of NOₓ from fuel nitrogen is more complex and a simple kinetic mechanism has not yet evolved. However, it is apparent that at ordinary combustion temperatures, fuel NO formation is much more rapid than thermal NO formation, and is much less temperature dependent (Pershing and Berkau 1972). This is probably because a N≡N bond does not have to be broken to form NO and it means that the standard NO abatement methods which depend primarily on peak temperature reduction (such as flue gas recirculation and water injection) are not effective.

In coal combustion it has been shown by Pershing, Martin and Berkau (1973) that ninety-five percent of the resulting NO emissions
arise from fuel NO and that those emissions are insensitive to flame
temperature and flue gas recirculation. Indeed the only known abate-
ment method for fuel NO is that of low excess air operation; yet this
is often difficult to achieve in practical pulverized coal combustion
systems. However, it is known that other combustion variables can
affect the conversion of fuel nitrogen to fuel NO (Armento and Sage
1973) and therefore it would appear that combustion modification still
offers the best opportunities for fuel NO reduction. It was the pur-
pose of this work to investigate further which variables are likely to
affect fuel NO formation from solid fuel combustion and to focus in
particular on variables associated with fuel characteristics.

Combustion Modelling

One of the objectives of combustion modelling is to gain in-
sight into the parameters that control the formation of NO in coal com-
bustion in the hope of being able to design meaningful experiments, to
interpret the data that is currently available, and to suggest prac-
tical abatement methods.

The chemical mechanisms of combustion depends strongly on the
physical processes involved in creating the environment in which the
chemistry takes place. Because of the low volatility of coal, char
and residual fuel oil, these fuels are not premixed with the combus-
tion air to form a gaseous mixture and combustion takes place in a
diffusion flame environment. Diffusion flames, however are very com-
plex phenomena and numerous approximation must be made to make the
problem tractable. Sternling and Wendt (1972) developed a model which
allowed droplet and particle combustion to be described in terms of three regimes as shown in Figure 1. The first regime occurs during rapid devolatilization and leads to a detached essentially premixed combustible mixture. The second regime is formed during periods of slow devolatilization and leads to an attached diffusion flame around the particle or droplet. After volatilization is completed the oxygen attacks the pyrolyzed surface directly and thus initiates the third regime, or char burnout of combustion.

At present there is little data that show how chemically bound nitrogen is distributed among the pyrolysis products. Sternling and Wendt (1972) using fragmentary data indicated the path of chemically bound nitrogen in coal combustion. This distribution is shown in Figure 2 where it can be seen that a significant portion of the nitrogen in the coal will not be volatilized but will appear in the char.

In this work we focus on the third regime of combustion and attempt to model the conversion of fuel nitrogen during the char burnout regime. Previous work in this area of fuel nitrogen conversion has been oriented to homogeneous gas phase kinetics (Axworthy and Shuman 1973) and pilot plant work (Martin and Berkau 1972a). Present studies (Axworthy and Shuman 1973) are yielding valuable insights into what happens to fuel nitrogen during the volatilization and pyrolysis regime of combustion. Field et al. (1967) has shown that in coal and
A. Totally Detached Flame. Rapid Mixing, Rapid Volatilization

Fuel-Rich Regions
Regions for Pyrolysis, Cracking
HCN, N, Pyrolysis Compounds Formed

B. Attached, Diffusion Flame. Pyrolysis Occurs in Fuel-Rich Region
Char is Being Formed

C. Char Burn-Out. Surface Combustion Occurs when Volatiles have Been Driven Out. CO Formed as Result of Surface Reaction of Carbon and O₂. This CO Burns Externally to the Solid Particle in a Diffusion Flame.

Figure 1. Three Regimes of Particle or Droplet Combustion
Figure 2. Tentative Diagram Showing Paths Taken by Fuel Nitrogen in Coal Combustion
coal char combustion, gas-solid reactions are important and thus may hold a key in understanding fuel nitrogen conversion to NO_x for solid fuels.

Ayling and Smith (1972) have shown that in the third regime of combustion, carbon is heterogeneously consumed by direct reaction with oxygen molecules to form CO. The CO is then oxidized homogeneously to CO_2 either in the particle pores or in the stagnant film surrounding the particle.

In the case of chemically bound nitrogen the same type of heterogeneous consumption by direct reaction with oxygen will form NO because it is hard to envisage nitrogen atoms bound in the char forming the N≡N bond directly when attacked by oxygen. Thus since this fuel nitrogen is a single atom, it can be expected to yield total conversion to NO_x at the particle surface. However measurements obtained by the Bureau of Mines are lower than those expected if all the fuel nitrogen were converted to NO (McCann 1973). This leads to the hypothesis that all the chemically bound nitrogen is heterogeneously converted to NO at the surface but some of this NO is homogeneously reduced back to N_2 in the fuel rich (diffusion flame) zone surrounding the particle or inside the particle. NO is therefore an intermediate product in the formation of N_2 from fuel nitrogen.

Gas-solid reactions, as used in catalyst theory, offer some aspects of a useful model since the yield of an intermediate depends strongly on particle characteristics. It is therefore reasonable to hypothesize that a similar situation exists in fuel nitrogen conversion during char combustion.
Since it is not clear whether the homogeneous reduction of NO to N₂ will occur in the pores or will include portions of the stagnant film surrounding the particle it is proposed to model the char burnout regime in two phases. First diffusion and reaction in a single pore is examined; then the processes occurring in the stagnant film surrounding the particle are modelled. The resulting models then serve to gain insight into the parameters controlling NO formation from fuel nitrogen in the char burnout regime.
CHAPTER 2

THEORETICAL MODEL

The salient features of the theoretical model developed are that carbon and fuel nitrogen are converted to carbon monoxide and to nitric oxide respectively at the particle surface and that further reactions to carbon dioxide and molecular nitrogen occur homogeneously either inside the particle pore or outside the particle surface in a stagnant film surrounding the particle. This model was then used to investigate the effects of particle characteristics and to isolate which types of critical information must be obtained experimentally in order to confirm results of the basic model hypothesis.

That fuel nitrogen should be converted to NO at the particle surface is intuitively reasonable since at the surface there is no kinetic route by which the N≡N bond can be formed. It is known (Field et al., 1967) that carbon is converted to CO, rather than CO$_2$, at the surface. Surface reaction of fuel nitrogen would alone lead to 100% conversion to NO, but this has seldom been observed (McCann et al., 1971). Therefore, it is certainly reasonable to postulate that some of the NO formed at the surface then reacts homogeneously with CO to be reduced partially to N$_2$. Wendt et al. (1972) have shown that NO can be reduced homogeneously in a fuel rich environment, a phenomenon they described as "reburning".
In the model presented here, "reburning" of NO to N\textsubscript{2} holds the key to explaining the partial conversion of fuel nitrogen to NO\textsubscript{x}.

The overall model, even in its simplest possible form, is therefore somewhat complex, involving diffusion of at least three species with coupled homogeneous and heterogeneous reactions between them. It is useful, however, to explore the model and the chemical reactions in more detail.

**Chemical Reactions**

Oxygen (O\textsubscript{2}) is believed to diffuse into the surface, either into a particle pore or to the particle surface where it reacts with the carbon (C) to form carbon monoxide (CO) according to Reaction I, Figure 3.

It was hypothesized also that all the chemically bound nitrogen (Fuel-N) is oxidized heterogeneously by oxygen at the surface into nitric oxide (NO) via Reaction II, Figure 3.

The carbon monoxide and nitric oxide diffuse back and react homogeneously to form carbon dioxide (CO\textsubscript{2}) and nitrogen (N\textsubscript{2}) through Reactions III and IV, Figure 3 where Reaction III is a gross representation of reburning, as described by Wendt et al. (1972).

The following assumptions were made in obtaining the simplified forms of Reaction I through IV, Figure 3:

1 - Reactions inside the char particle and on the char surface are important.

2 - The reactions were of global type, no reverse reactions were considered.
3 - Simplified mechanisms were applicable.

The first assumption is based on data by Sternling and Wendt (1972) and McCann et al. (1971) where it is shown that in the combustion of coal and heavy residual fuel oil substantial quantities of chemically bound nitrogen are not volatilized but carried through into the char. The second assumption was necessary to keep the model simple. The simplified model was designed to describe merely the salient features of the kinetic mechanisms rather than all of the details involving free radicals and unstable species. Validity of these approximations can only be ultimately verified in conjunction with experimental data.

Reverse reactions were neglected by using the following reasoning. In Reaction I, Figure 3, there is little possibility that carbon monoxide will dissociate into oxygen and carbon without requiring a great amount of energy. The same argument can be applied to Reaction II for the dissociation of nitrogen monoxide into oxygen and nitrogen. In the case of Reaction III, the possibility that carbon dioxide will react with nitrogen to produce NO and CO is not likely since a great amount of energy would be necessary to break the triple bond of nitrogen. The large activation energy for the dissociation of carbon dioxide into carbon and oxygen in Reaction IV makes this reaction unlikely to take place. Thus it is justified that the reverse reactions were not considered in modelling the production of NO in a burning char particle.
Figure 3. Chemical Reactions

\[
\begin{align*}
C + \frac{1}{2} O_2 & \xrightarrow{K_1} CO \\
\text{fuel } N + \frac{1}{2} O_2 & \xrightarrow{K_2} NO \\
NO + CO & \xrightarrow{K_3} \frac{1}{2} N_2 + CO_2 \\
CO + \frac{1}{2} O_2 & \xrightarrow{K_4} CO_2
\end{align*}
\]

(K)h

Figure 4. Rate Coefficients

\[
\begin{align*}
K_1(T) &= A_s \exp \left( - \frac{E_1}{RT} \right) \quad \text{cm}^3 \text{sec}^{-1} \\
K_2(T) &= 8.571 \times 10^{-3} \ K_1(T) \quad \text{cm}^3 \text{sec}^{-1} \\
K_3(T) &= \frac{1.34 \times 10^4}{\rho} \quad \text{cm}^3 \text{gm mole}^{-1} \text{sec}^{-1} \\
K_4(T) &= \sqrt{0.1} \rho \ K_0 \exp \left( - \frac{E_2}{RT} \right) \quad \text{cm}^{1.5} \text{gm mole}^{1/2} \text{sec}^{-1}
\end{align*}
\]
Rate Coefficients

The rate coefficient, $K_1$, for Reaction I, Figure 3, was obtained from the work by Field et al. (1967) where the surface reaction rate is defined by Equation 1.

$$K_s = A_0 \exp \left[ -\frac{E_1}{RT} \right] \quad (1)$$

where:
- $K_s$: Surface reaction rate coefficient
- $A_0$: Surface reaction rate constant
- $E_1$: Activation Energy
- $R$: Gas constant
- $T$: Temperature

Thus the rate of reaction for the surface reaction in (cm/sec) is defined by Equation 2

$$K_1 = K_s RT \quad (2)$$

substituting $K_s$ from Equation 1 in Equation 2, Equation a, Figure 4 is obtained which defines the rate coefficient $K_1$. No published data exists on the surface rate coefficient of fuel nitrogen oxidation.

Thus the rate coefficient $K_2$ for Reaction II was estimated by assuming that fuel nitrogen is uniformly distributed throughout the char and that coal char contains about 1% weight of fuel nitrogen. Thus $K_2$ should be of the order of 1% of $K_1$ with an appropriate adjustment to
account for the different molecular weights of carbon and nitrogen. To account for the fact that the percent of fuel nitrogen in the coal may be different from 1% the factor of q was introduced. This factor is equal to the percent of fuel nitrogen in the coal divided by 0.01. Equation 3 results from this approximation

$$K_2 = 5.87 \times 10^{-3} q K_1(T) \frac{cm}{sec}$$ (3)

In this work the value for q is 1. Thus Equation b, Figure 4 was obtained.

The rate coefficient, $K_3$, for Reaction III was obtained by manipulating data by Sarofim et al.(1973) as shown in Figure 5 and by using the half time method described by Levenspiel (1962). This was accomplished as follows:

Defining the rate of consumption of NO from Reaction III, Figure 3, Equation 4 was obtained

$$R_{NO} = - \frac{d[NO]}{dt} = K^* [CO][NO]$$ (4)

Defining an effective reaction rate and substituting in Equation 4

$$K_{eff} = K^*[CO]$$ (5)

$$- \frac{d[NO]}{dt} = K_{eff} [NO]$$ (6)
Figure 5. Concentration Profile of Nitric Oxide Normalized with the Maximum Concentrations. (Sarofim et al., 1973)
The differential equation in Equation 7 has the following Boundary Conditions:

\[ t = 0 \quad [\text{NO}] = [\text{NO}]_0 \quad (8) \]

\[ t = t_{1/2} \quad [\text{NO}] = \frac{1}{2} [\text{NO}]_0 \quad (9) \]

Integrating Equation 7 and evaluating the constants of integration using Equations 8 and 9, Equation 10 was obtained.

\[ K_{\text{eff}} = \frac{\ln 2}{t_{1/2}} \quad (10) \]

The value of \( t_{1/2} \) was obtained from Figure 5

\[ t_{1/2} = 0.35 \times 10^{-3} \text{ sec.} \]

Substituting \( t_{1/2} \) in Equation 10

\[ K_{\text{eff}} = 3.961 \times 10^3 \frac{1}{\text{sec}} \quad (11) \]

It is apparent that the rate of Reaction III must depend on the concentration of CO present. As a first approximation it was assumed that in the experiment by Sarofim et al. (1973) the
concentration of CO was obtained by a stoichiometric CO/air mixture at the flame conditions. This led to Equation c, Figure 4. It must be pointed out that in absence of data to the contrary, it was assumed that $K_3$ is not a strong function of temperature.

The rate coefficient $K_4$ for Reaction IV was obtained from Howard, Williams and Fine (1972) where the global reaction rate is given as:

$$R_{CO} = K_0 \exp \left( -\frac{E_2}{RT} \right) [CO]^{1/2} [O_2]^{1/2} [H_2O]^{1/2}$$  (12)

Since the concentration of H$_2$O is not known the assumption that there is a constant mole fraction of water of 10% was made, thus:

$$[H_2O] = 0.1 \rho$$  (13)

where

$$\rho = \frac{P}{RT}$$  (14)

Substituting Equation 13 in Equation 12, Equation 15 is obtained

$$R_{CO} = \sqrt{0.1\rho} K_0 \exp \left( -\frac{E_2}{RT} \right) [CO]^{1/2} [O_2]^{1/2}$$  (15)

thus $K_4$ is defined in Equation d, Figure 4. The values used for Equations a, b, c, and d are shown in Table 1. The effect of temperature on the kinetic rate coefficients are shown in Figures 6 and 7.
### Table 1. Values Used for Calculating the Rate Coefficient and Diffusivities

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Unit</th>
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<tbody>
<tr>
<td>As</td>
<td>725.833</td>
<td>gm mole cm²-sec-atm</td>
</tr>
<tr>
<td>E₁</td>
<td>35,100</td>
<td>cal gr mole</td>
</tr>
<tr>
<td>K₀</td>
<td>1.3 x 10¹⁴</td>
<td>cc gm mole-sec</td>
</tr>
<tr>
<td>E₂</td>
<td>30,000</td>
<td>cal gm mole</td>
</tr>
<tr>
<td>A₁</td>
<td>3.75903 x 10⁵</td>
<td>cm² sec (°K)¹·5</td>
</tr>
<tr>
<td>A₂</td>
<td>3.948571 x 10⁻⁵</td>
<td>cm² sec (°K)¹·5</td>
</tr>
<tr>
<td>A₃</td>
<td>3.871207 x 10⁻⁵</td>
<td>cm² sec (°K)¹·5</td>
</tr>
<tr>
<td>R</td>
<td>1.986</td>
<td>cal gm mole °K</td>
</tr>
</tbody>
</table>
Figure 6. Effect of Temperature on Kinetic Rate Coefficient $K_1$ and $K_4$. 
Figure 7. Effect of Temperature on Kinetic Rate Coefficients $K_2$ and $K_3$. 
Of the four rate coefficients determined from the literature the most uncertain is the value calculated for $K_3$, Equation c, Figure 4, that is, the rate that describes the reduction of NO to $N_2$. It was therefore felt necessary to investigate sensitivities of the results obtained to the value of $K_3$ used.

**Diffusion Coefficients**

The assumption that all the species are diffused in nitrogen was made. This is justified from the fact that in atmospheric combustion there is 79% of nitrogen present. The diffusivities will be expressed as a function of temperature taking the form of Equation 16

$$D_{ij} = A_i T^{1.5}$$  \hspace{1cm} (16)

$i = \text{specie } i$

$j = N_2$

In order to determine $A$, the diffusivity of the specie must be known at a given temperature. To obtain this value the Chapman-Enskong theory for low density gases described in Bird, Stewart and Lightfoot (1960) was used. The general formula for diffusion as a function of temperature is given by Equation 17

$$D_{ij} = \frac{1.8583 \times 10^{-3} \sqrt{T^3 \left( \frac{1}{M_i} + \frac{1}{M_j} \right)}}{\sigma_{ij}^2 \Omega_{ij}}$$  \hspace{1cm} (17)
where

\[ M_i, M_j : \text{Molecular weights} \]
\[ \sigma_{ij} : \text{Collision diameter} \]
\[ \Omega_{Dij} : \text{Dimensionless function of temperature and of intermolecular potential.} \]

The collision diameter is defined in Equation 18

\[ \sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j) \quad (18) \]

The values for \( \Omega_{Dij} \) are given by Bird et al. (1960) as a function of \( kT/\varepsilon_{ij} \) where:

\[ \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad (19) \]

Using the values given by Bird et al. (1960) and Equations 16 through 19 the values for the \( A_i \)'s were obtained. These values are shown in Table 1.

**One Dimensional Pore Model**

The interaction of chemical kinetics and diffusion in a single char particle pore were studied to determine the effect of pore radius and pore length in the net production of NO within a burning char particle. Using the chemical reactions from Figure 3 and a shell balance on the pore of Figure 8 the following equations are obtained:
Figure 8. One Dimensional Pore Model
for oxygen

\[
\text{Input} - \text{Output} + \text{Generation} = 0
\]  

(20)

\[
\pi r^2 N A_x \bigg|_x - \pi r^2 N A_x \bigg|_{x+\Delta x} + 2\pi r \Delta x R_1 + \pi r^2 \Delta x R_4 = 0
\]  

(21)

dividing by \(\pi r^2\) and \(\Delta x\) and taking the limit as \(\Delta x \to 0\)

\[
- \frac{d}{dx} \left( N_{Ax} \right) + \frac{2}{r} R_1 + R_4 = 0
\]  

(22)

Using Fick's second law that defines the flux resulting from diffusion

\[
N_{Ax} = - D_1 \frac{dC_1}{dx}
\]  

(23)

Substituting Equation 23 into Equation 22

\[
D_1 \frac{d}{dx} \left( \frac{dC_1}{dx} \right) + \frac{2}{r} R_1 + R_4 = 0
\]  

(24)

where the \(R_i\)'s defines the rate of formation of component \(i\)

\[
R_1 = R_a + R_b
\]  

(25)

\[
R_4 = R_d
\]  

(26)

The rate of depletion of oxygen is obtained from Figure 3.

This figure shows that \(O_2\) is being consumed in Reactions I, II and IV.

The amount of \(O_2\) used in Reaction II is relatively small compared to
the amount used in Reactions I and IV. Hence $R_b$ was set equal to zero. Thus

$$R_1 = -\frac{K_1}{2} C_1$$  \hspace{1cm} (27)

$$R_4 = -\frac{K_4}{2} C_2 C_1^{\frac{1}{2}}$$  \hspace{1cm} (28)

Substituting Equations 27 and 28, Equation a, Figure 9, was obtained. The boundary conditions for Equation a are defined in Equations b and c, Figure 9.

Similar procedure was used in the case of carbon monoxide and nitric oxide. The equations are shown in Figure 9. It can be seen that in the model the conservation equation for NO is coupled to the concentration profiles for CO and $O_2$ while the CO, and $O_2$ profiles are not affected by the NO profile. This allows substantial simplifications to be made in solving the equations.

A dimensional analysis was done on the differential equations describing the pore, Equations a to i, Figure 9, to find a dimensional group which will characterize the behavior of the system. The following definitions are used.

$$\psi_1 = \frac{C_1}{C_{O_1} - C_{L_1}}$$  \hspace{1cm} (29)

$$\psi_2 = \frac{C_2 - C_{O_2}}{C_{L_2} - C_{O_2}}$$  \hspace{1cm} (30)
For oxygen

\[ D_1 \frac{d^2 C_1}{dx^2} - \frac{K_1}{r} C_1 - \frac{K_4}{2} C_2 C_1^{\frac{1}{2}} = 0 \]  \hspace{1cm} (a)

\[ x = 0 \quad \frac{dC_1}{dx} = 0 \]  \hspace{1cm} (b)

\[ x = L \quad C_1 = C_{01} \]  \hspace{1cm} (c)

For carbon monoxide

\[ D_2 \frac{d^2 C_2}{dx^2} + \frac{2}{r} K_1 C_1 - K_4 C_2 C_1^{\frac{1}{2}} = 0 \]  \hspace{1cm} (d)

\[ x = 0 \quad \frac{dC_2}{dx} = 0 \]  \hspace{1cm} (e)

\[ x = L \quad C_2 = 0 \]  \hspace{1cm} (f)

For nitric oxide

\[ D_3 \frac{d^2 C_3}{dx^2} + \frac{2}{r} K_2 C_1 - K_3 C_2 C_3 = 0 \]  \hspace{1cm} (g)

\[ x = 0 \quad \frac{dC_3}{dx} = 0 \]  \hspace{1cm} (h)

\[ x = L \quad C_3 = 0 \]  \hspace{1cm} (i)

Figure 9. Second Order Differential Equations and Boundary Conditions for Pore Model
\[ \psi_3 = \frac{C_3 - C_{03}}{C_{L3} - C_{03}} \quad (31) \]

\[ \alpha_1 = C_{01} - C_{L1} \quad (32) \]

\[ \alpha_2 = C_{L2} - C_{02} \quad (33) \]

\[ \alpha_3 = C_{L3} - C_{03} \quad (34) \]

\[ \eta = \frac{x}{L} \quad (35) \]

Substituting Equations 29 through 35 in Equation a, Figure 9, we obtain

\[ \frac{d^2\psi_1}{d\eta^2} - \frac{L^2}{rD_1} K_1 \psi_1 - \frac{\alpha_2 L^2 K_4}{2D_1 \alpha_1^{1/2}} \psi_2 \psi_1^{1/2} = 0 \quad (36) \]

Grouping terms in order to obtain a dimensionless equation we get

\[ h_{1p} = \frac{L^2 K_1}{rD_1} \quad (37) \]

\[ h_{2p} = \frac{\alpha_2 L K_4}{2D_1 (\alpha_1^{1/2}/L)} \quad (38) \]
Equation 36 becomes

\[ \frac{d^2 \psi_1}{d\eta^2} - h_1 p \, \psi_1 - h_2 p \, \psi_2 \psi_1^{1/2} = 0 \]  

With the following boundary conditions

\[ \eta = 0 \quad \frac{d\psi_1}{d\eta} = 0 \]  
\[ \eta = 1 \quad \psi_1 = 1 \]  

The same procedure was used on Equations d through i in Figure 9. The following equation was obtained for carbon monoxide.

\[ \frac{d^2 \psi_2}{d\eta^2} + h_3 p \, \psi_1 - h_4 p \, \psi_2 \psi_1^{1/2} = 0 \]  

\[ \eta = 0 \quad \frac{d\psi_2}{d\eta} = 0 \]  
\[ \eta = 1 \quad \psi_2 = 1 \]  

For nitric oxide

\[ \frac{d^2 \psi_3}{d\eta^2} - h_5 p \, \psi_2 \psi_3 + h_5 p \, \psi_1 = 0 \]  

\[ \eta = 0 \quad \frac{d\psi_3}{d\eta} = 0 \]
where

\[ h_{3p} = \frac{2L\alpha_1 K_1}{\tau D_2 (\alpha_2 / L)} \]  

(48)

\[ h_{4p} = \frac{L\alpha_1 K_4}{(D_2 / L)} \]  

(49)

\[ h_{5p} = \frac{L\alpha_2 K_3}{(D_3 / L)} \]  

(50)

\[ h_{6p} = \frac{2L K_2}{\tau D_3 (\alpha_3 / L)} \]  

(51)

where \( h_i \)'s are the dimensionless groups that characterize the behavior of the system, \( h_i \)'s are called the Thiele parameters.

Multiplying and dividing Equation 37 by \( \pi \tau \) we obtain

\[ h_{1p} = \frac{\pi \tau L K_1}{\pi \tau^2 (D_1 / L)} \]  

(52)

or

\[ \frac{h_{1p}}{\text{surface reaction rate}} = \frac{1}{\text{diffusion rate}} \]  

(53)

From Equations 52 and 53 it can be concluded that small values of \( h_{1p} \) implies that the capability of the system to diffuse is much greater than the capability of the system to react, thus the system is reaction controlled and the concentration of species \( i \) inside the pore
will approach that of the pore mouth. Large values of $h_{ip}$ implies that the capability of the system to react chemically is large compared to the capability of the system to diffuse, thus the system is diffusion controlled. The concentration of species $i$ will not be the same as the concentration of $i$ at the beginning of the pore or the film. (Petersen 1965)

**One Dimensional Film Model**

The interaction of chemical kinetics and diffusion in a stagnant film surrounding a char particle were studied to determine the effect of particle size and film thickness in the conversion of fuel nitrogen to NO. Using the reactions from Figure 3 and a shell balance on the film in Figure 10 the following equations are obtained:

For oxygen:

$$\text{Input} - \text{Output} + \text{Generation} = 0 \quad (54)$$

$$4\pi r^2 N_{Ar} |r - 4\pi (r+\Delta r)^2 N_{Ar} |r+\Delta r + 4\pi r^2 \Delta r R_4 = 0 \quad (55)$$

Dividing by $4\pi \Delta r$ and taking the limit as $\Delta r \to 0$

$$\frac{d}{dr} (r^2 N_{Ar}) + r^2 R_4 = 0 \quad (56)$$

Using Fick's Second Law

$$N_{Ar} = -D_1 \frac{dC_1}{dr} \quad (57)$$
Figure 10. One Dimensional Film Model
Substituting Equation 57 in Equation 56

\[ \frac{d}{dr} \left( r^2 D_1 \frac{dC_1}{dr} \right) + r^2 R_4 = 0 \]  \hspace{1cm} (58)

Substituting Equation 28 in Equation 58 and defining the boundary conditions, Equations a, b, and c, Figure 11 are obtained. A similar procedure was used in the case of carbon monoxide and nitric oxide, resulting in Equations d through i, Figure 11.

A dimensional analysis was performed on Equations a through i in Figure 11. The same type of definitions used in the pore model were used here with the following definitions added:

\[ \phi = \frac{r-R1}{RF-RI} \]  \hspace{1cm} (59)

\[ \delta = RF - RI \]  \hspace{1cm} (60)

\[ \zeta(\phi) = (\delta \phi + RI) \]  \hspace{1cm} (61)
For oxygen

\[ \frac{D_1}{2} \frac{d^2C_1}{dr^2} + \frac{2}{r} \frac{D_1}{dC_1} \frac{dC_1}{dr} - \frac{K_4}{2} C_2 C_1^{1/2} = 0 \]  

(a)

\[ r = RI \quad \frac{dC_1}{dr} = \frac{K_1 C_1}{2D_1} \]  

(b)

\[ r = RF \quad C_1 = CO_1 \]  

(c)

For carbon monoxide

\[ \frac{D_2}{2} \frac{d^2C_2}{dr^2} + \frac{2}{r} \frac{D_2}{dC_2} \frac{dC_2}{dr} - K_4 C_2^{1/2} = 0 \]  

(d)

\[ r = RI \quad \frac{dC_2}{dr} = - \frac{K_1 C_1}{D_2} \]  

(e)

\[ r = RF \quad C_2 = 0 \]  

(f)

For nitric oxide

\[ \frac{D_3}{2} \frac{d^2C_3}{dr^2} + \frac{2}{r} \frac{D_3}{dC_3} \frac{dC_3}{dr} - k_3 C_2 C_3 = 0 \]  

(g)

\[ r = RI \quad \frac{dC_3}{dr} = - \frac{K_2 C_2}{D_2} \]  

(h)

\[ r = RF \quad C_3 = 0 \]  

(i)

Figure 11. Second Order Differential Equations for Film Surrounding the Particle
The dimensionless equations obtained are shown in Figure 12. The definition of $h_{if}$ are shown in Figure 13. The same type of discussion used in the pore model is valid for the Thiele parameter in the film model. It can be shown that $C_1$ and $C_2$ can be related as follows:

\[
\frac{d}{dr} \left( r^2 \frac{dC_1}{dr} \right) - \frac{K_4}{2} C_2 C_1^{1/2} = 0
\]  
(62)

\[
\frac{d}{dr} \left( r^2 \frac{dC_2}{dr} \right) - K_4 C_2 C_1^{1/2} = 0
\]  
(63)

Multiplying Equation 62 by 2 and subtracting Equation 63 from Equation 62

\[
\frac{d}{dr} \left[ r^2 \left( \frac{d^2C_1}{dr^2} - \frac{dD_2C_2}{dr} \right) \right] = 0
\]  
(64)

defining

\[
\theta = 2D_1C_1 - D_2C_2
\]  
(65)

hence

\[
\frac{d\theta}{dr} = \frac{dD_1C_1}{dr} - \frac{dD_2C_2}{dr}
\]  
(66)

Substituting Equation 66 in Equation 64
For oxygen

\[ \frac{1}{[\zeta(\phi)]^2} \frac{d}{d\phi} \left[ [\zeta(\phi)]^2 \frac{d\psi_1}{d\phi} \right] - h_{1f} \psi_2 \psi_1^{1/2} = 0 \]  

(a)

\[ \phi \rightarrow 0 \quad \frac{d\psi_1}{d\phi} = \frac{\delta K_1 \psi_1}{D_1} \]  

(b)

\[ \phi \rightarrow 1 \quad \psi_1 = 1 \]  

(c)

For carbon monoxide

\[ \frac{1}{[\zeta(\phi)]^2} \frac{d}{d\phi} \left[ [\zeta(\phi)]^2 \frac{d\psi_2}{d\phi} \right] - h_{2f} \psi_2 \psi_1^{1/2} = 0 \]  

(d)

\[ \phi \rightarrow 0 \quad \frac{d\psi_2}{d\phi} = - \frac{\delta \alpha_1 K_1 \psi_1}{D_2 \alpha_2} \]  

(e)

\[ \phi \rightarrow 1 \quad \psi_2 = 1 \]  

(f)

For nitric oxide

\[ \frac{1}{[\zeta(\phi)]^2} \frac{d}{d\phi} \left[ [\zeta(\phi)]^2 \frac{d\psi_3}{d\phi} \right] - h_{3f} \psi_2 \psi_3 = 0 \]  

(g)

\[ \phi \rightarrow 0 \quad \frac{d\psi_3}{d\phi} = - \frac{\delta \alpha_1 K_2 \psi_1}{D_3 \alpha_3} \]  

(h)

\[ \phi \rightarrow 1 \quad \psi_3 = 1 \]  

(i)

Figure 12. Dimensionless Equations for Film Model
For oxygen

\[ h_{1f} = \frac{\pi r^2 \delta \alpha \alpha_2 K_4}{2\pi r^2 D_1 (\alpha_1 \frac{\delta}{r})} \]  

(a)

For carbon monoxide

\[ h_{2f} = \frac{\pi r^2 \delta \alpha_1 \alpha_2 K_4}{\pi r^2 D_2 (\alpha_2 \delta)} \]  

(b)

For nitric oxide

\[ h_{3f} = \frac{\pi r^2 \delta \alpha_2 K_3}{\pi r^2 (D_3 \delta)} \]  

(c)

Figure 13. Thiele Parameters for Film Model
\[ \frac{d}{dr} \left( r^2 \frac{d\theta}{dr} \right) = 0 \quad (67) \]

Substituting Equations b and e, Figure 11 on Equation 66 we obtain

\[ \frac{d\theta}{dr} \bigg|_{r = RI} = 2K_1C_1 \quad (68) \]

\[ \theta \bigg|_{r = RF} = 2D_1C_1 + D_2C_2f \quad (69) \]

Equation 67 can be integrated

\[ \frac{d\theta}{dr} = \frac{B_1}{r^2} \quad (70) \]

Integrating Equation 70 once again

\[ \theta = -\frac{B_1}{r} + B_2 \quad (71) \]

Evaluating \( B_1 \) and \( B_2 \) using Equations (68 and 69)

\[ B_1 = 2RI^2K_1C_1 \quad (72) \]

\[ B_2 = \frac{B_1}{RF} + \theta_f \quad (73) \]

Substituting Equations 72 and 73 in Equation 71
\[
\theta = -\frac{2RI^2K_1C_1}{r} + \frac{2RI^2K_1C_1}{RF} + \theta_f
\]  

(74)

rearranging and solving for \( C_2 \) at \( r = RI \)

\[
C_2 = \frac{C_1}{D_2} \left[ 2D_1 - 2K_1RI^2 \left( \frac{1}{RF} - \frac{1}{RF} \right) \right] + \theta_f
\]  

(75)

Thus, \( C_1 \) and \( C_2 \) are simply related throughout their profiles, \( C_2 \) can be calculated from \( C_1 \). This allows the solution to these equations to be significantly simplified.

In order to obtain the boundary conditions in Equations f and i, Figure 7 and Equations f and i, Figure 9, it was assumed that the velocity of the gas is sufficiently high to remove the products as soon as they are formed. Thus the quantity of interest for the pore model is the flux of NO at the pore mouth. In the film model the quantity of interest is the net percent conversion of fuel nitrogen to NO. Since all the fuel nitrogen is converted to NO at the surface with subsequent reduction to \( N_2 \) occurring in the stagnant film, the net percent of fuel nitrogen converted can be calculated from the ratio of the flow of NO leaving the film to the flow of NO leaving the surface:

\[
\% \text{ Conv} = \left[ 1 - \frac{(\text{flux}_f)_{RF}^2}{(\text{flux}_i)_{s,RF}^2} \right] \times 100
\]  

(76)

Numerical Techniques

To solve the system of coupled nonlinear second order differential equations shown in Figures 7 and 9 a numerical integration method
is required. However the boundary conditions used in the differential equations, Equations a, d and g, Figure 7, and Equations a, d, and g, Figure 9, make the system a boundary value problem. Most numerical techniques for solving ordinary differential equations are applicable strictly only to initial value problems. The approach utilized here is to pose the problem as an initial value problem, and then to guess one of the initial conditions. An optimization algorithm then optimizes the initial guesses to fit the other for boundary conditions.

The numerical integrations are done using the Runge-Kutta-Gill fourth order algorithm described by Carnahan, Luther and Wilkes (1969). The Hooke-Jeeves optimization method described by Beveridge and Schechter (1970) is used to solve the boundary value problem. This method finds the minimum of a multivariable constrained nonlinear function.

The boundary value nature of the problem is changed to that of an initial value problem, by guessing the initial concentration for O₂ and CO at x = 0. The initial gradient was then specified as shown in Equations b, e and h, Figure 7 for the pore model, and Equations b, e and h, Figure 9 for the film model. Then the numerical integration is performed and a check is made to determine whether the other boundary conditions are met within a certain tolerance. If not then the initial guesses are changed until the far boundary conditions are satisfied. To use the Hooke-Jeeves method a function to be optimized must be defined. In this case the function represents the deviation'
of the calculated values at the far boundary to those specified by the far boundary conditions. This residual function is defined in Equation 77:

\[ \text{RES} = \left( \frac{C_1^* - C_{1f}}{C_{1f}} \right)^2 + \left( \frac{C_2^* - C_{2f}}{C_{2f}} \right)^2 + \left( \frac{C_3^* - C_{3f}}{C_{3f}} \right)^2 \]  

(77)

when

\[ C_{2f} \neq 0 \quad ; \quad C_{3f} \neq 0 \]

or

\[ \text{RES} = \left( \frac{C_1^* - C_{1f}}{C_{1f}} \right)^2 + C_{2*}^2 + C_{3*}^2 \]  

(78)

when

\[ C_{2f} = C_{3f} = 0.0 \]

Thus there are three variables, \( C_1^0, C_2^0 \) and \( C_3^0 \). By inspection, Equations a and d, Figure 7 are coupled while Equation g is essentially uncoupled. Thus while the concentration of NO depends on the concentration of CO, the concentration of CO and \( O_2 \) do not depend on that of NO. Hence there are two variables (\( C_1^0, C_2^0 \)) to be optimized simultaneously. Once the solution is obtained for the two variables then
the third variable $C_3^0$ is optimized alone. Thus Equation 77 becomes

$$\text{RES}^* = \left( \frac{C_1^* - C_{1f}}{C_{2f}} \right)^2 + \left( \frac{C_2^* - C_{2f}}{C_{2f}} \right)^2$$  \quad (79)$$

when $C_{2f} \neq 0$

or

$$\text{RES}^* = \left( \frac{C_1^* - C_{1f}}{C_{1f}} \right)^2 + C_{2f}^2$$  \quad (80)$$

when

$$C_{2f} = 0$$

$$\text{RES}^{**} = \left( \frac{C_3^* - C_{3f}}{C_{3f}} \right)^2$$  \quad (81)$$

when

$$C_{3f} \neq 0$$

or

$$\text{RES}^{**} = C_{3f}^2$$  \quad (82)$$

when

$$C_{3f} = 0$$
Optimization for the film model is somewhat simpler since as shown by Equation 75, \( C_i^0 \) is directly related to \( C_2^0 \) and so only one concentration needs to be optimized. The residual functions to be minimized remain the same as those used for the pore model.

To obtain an acceptable solution, the following constrain must be applied:

1. \( C_1, C_2 \) and \( C_3 \) cannot be negative anywhere.
2. \( C_1, C_2 \) and \( C_3 \) must be less than the value defined by Equation 14.
3. \( \text{AL}_2 \) and \( \text{AL}_3 \) must be 0.

\( \text{AL}_2 \) and \( \text{AL}_3 \) represent positions where the concentrations have unrealistic values causing integration instabilities. \( \text{AL}_2 \) is used in the optimization of \( C_1^0 \) and \( C_2^0 \). \( \text{AL}_3 \) is used in the optimization of \( C_3^0 \). The values of \( \text{AL}_2 \) and \( \text{AL}_3 \) were introduced because otherwise numerical instabilities in the numerical integration could occur.

These requirements introduce constraints in the residual function making it uneven; i.e., there are several ridges in the residual function contour map. Thus it was found that the method of Hookes-Jeeves works reasonably well in the case of one variable. However when more than one variable is involved the effectiveness of this method was found to be dependent on the problem to be solved.

Since the differential equations on Figure 7 and 9 are decoupled, two sequential computer programs are needed for either the pore or the film model. For the pore model the first program, CHARPCO, uses the method of Hookes-Jeeves to obtain the best value of \( C_1^0 \) and \( C_2^0 \) by minimizing the residual function defined in Equation 79. The film
model analog to this is the program CHARFCO which optimizes \( C_1^0 \). The second program, CHARPNO used the same method as CHARPCO to optimize \( C_3^0 \), by minimizing the residual function defined in Equation 81, once \( C_1^0 \) and \( C_2^0 \) have been found. This method is also used in the case of the film model and is called CHARFNO.

The method of Hooke-Jeeves will change the value of the initial guess for \( C_1^0 \) and \( C_2^0 \) until a small value of the residual function, Equation 77, is obtained. During this process if \( A12 \) and \( AL3 \) happens to be different from 0 the residual function is redefined as:

\[
\text{RES} = 1.0 \times 10^{100}
\]  

(83)

to prevent this from occurring again.

The general procedure was to solve the differential equations using ten steps for the Runge-Kutta-Gill algorithm. When a small value of the residual function is found, the number of steps is increased to one hundred and the same procedure is used until the value of the residual function is small. The ten steps are used in order to obtain a better initial guess for \( C_1^0 \) and \( C_2^0 \) utilizing short computation time since the number of calculations are fewer. Once the residual function is smaller then the steps are increased to one hundred, to obtain an accurate solution that meets all the constraints previously described. Before the optimization algorithm can be used, several precautions are taken. The first is that the initial guess for \( C_1^0 \) and \( C_2^0 \) are within bounds; that is they are always positive and are not greater than \( \rho \).
defined in Equation 14. The second precaution is to integrate Equations a, d, and g, Figure 7, and Equations a, d, and g, Figure 9, and to check for non zero values of AL2 and AL3. In the event that AL2 or AL3 are non zero, the guessed value for C0 is reduced by a factor of ten, (in the case of CHARPCO). Reduction of the value of C0 makes the initial slope of C2 smaller and repetition of this process eventually leads to a zero value for AL2. In the case of CHARPNO and CHARFNO the initial guessed value for C0 is altered until the slope is reduced and AL3 is brought to zero. In CHARFCO the value of C0 is multiplied by 0.80 because of C1 and C2 are coupled and a large change in C1 causes further instabilities. In the event that after one thousand iterations there is no convergence in finding a minimum in the optimization scheme the program will only run for ten more iterations thus producing enough output to allow the cause for divergence to be determined after which the program exits.

To check for truncation errors involved in Runge-Kutta-Gill numerical integration method, the following procedure was used. The step size was decreased from $1.0 \times 10^{-2}$ to $2.0 \times 10^{-3}$ and the number of points was increased from ten to fifty. The difference between the initial concentration of O2 was 1.6 percent and the difference in the final concentration of O2 using both methods was 0.3 percent. A new step size of $1.0 \times 10^{-4}$ was chosen so the number of points in the interval was increased from fifty to one thousand. The difference using this step size and $2.0 \times 10^{-3}$ was zero for the initial concentration
of O₂ while the difference in the final concentration was $5.0 \times 10^{-3}$. Thus it was concluded that the solution obtained was independent of the step size.

The general flow chart for program CHARFCO for the film model is shown in Figure 14. The same logic is used in the pore model and CHARFNO. A detailed description of the role of the program and the subroutines is described in Table 2. Program CHARFNO and a set of results are shown in Appendix A.
Figure 14. Flow Chart for Program CHARFCO
Figure 14 Continued
Figure 14 Continued
<table>
<thead>
<tr>
<th>Subroutines</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHARFCO</td>
<td>Read in the data. It calls subroutines INITIAL, FSOPT, OBJFN, NEWPRT, SUPFIN, SMCUT, RKGS. Writes out the residual function calculated with ten steps and one hundred steps, C1 and C2. Punch output to be used in CHARFNO. Calculates the new guesses to be used in OBJFN.</td>
</tr>
<tr>
<td>INITIAL</td>
<td>This subroutine calculates the parameters described in Figure 4 and evaluates the parameters that will not change during the integration and optimization. It sets the initial guesses for C1 and C2.</td>
</tr>
<tr>
<td>FSOPT</td>
<td>This subroutine calls RKGS to check for AL2. In the case that AL2 is not zero it calls CHANG02 to modify the value of C1. It will do this until AL2 is zero.</td>
</tr>
<tr>
<td>OBJFN</td>
<td>This subroutine calculates the residual function using C1 and C2 from CHARFCO. It calls RKGS to calculate C1f and C2f. It checks for AL2 if not zero it uses Equation 77. It calls PRNTOUT if extensive debugging is required. It calls PRNTSTOP.</td>
</tr>
<tr>
<td>NEWPRT</td>
<td>It provides output for the ten steps if extensive output is desired. It calls RKGS.</td>
</tr>
</tbody>
</table>
### Table 2, Continued

<table>
<thead>
<tr>
<th>Subroutines</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUPFIN</td>
<td>It makes the necessary calculations to change the steps from ten to one hundred.</td>
</tr>
<tr>
<td>RKGS</td>
<td>It uses the Runge-Kutta-Gill algorithm to solve the differential equations. It calls FCTN.</td>
</tr>
<tr>
<td>PRNTOUT</td>
<td>It prints out every calculation if the program has to be debugged.</td>
</tr>
<tr>
<td>FCTN</td>
<td>The differential equations to be solved are defined in this subroutine.</td>
</tr>
<tr>
<td>SMCUT</td>
<td>This is an entry in subroutine FSOPT. It does the same operation as FSOPT but for one hundred steps.</td>
</tr>
<tr>
<td>PRTSTOP</td>
<td>It is an entry in subroutine NEWPRT. It calls RKGS to print final values in the integration and stop the program.</td>
</tr>
</tbody>
</table>
CHAPTER 3

RESULTS

Two sets of results are presented here. Those obtained for the pore model, programs CHARPCO and CHARPNO, and from the film model, programs CHARFCO and CHARFNO.

Pore Model

A measure of the net emission of NO from a pore of a burning char particle is given by the flux of NO leaving the pore mouth. In this section the effect of temperature, pore length, pore radius and the value of $K_3$ on the fluxes of NO and CO and the concentration profiles is described.

Effect of Temperature

This effect of temperature on the concentration profiles of $O_2$, CO and NO is shown in Figures 15 and 16. Figure 15 shows that at $1000^\circ K$ these profiles are smooth and that diffusion and chemical reaction takes place along the length of the pore. It can also be seen that the concentration of NO goes through a maximum at a distance of 0.0734 cm along the pore. Figure 16 shows that at temperatures higher than $1000^\circ K$ the concentration of oxygen goes very rapidly down to a very small value at the pore mouth. Essentially the gradient of $O_2$ is infinite and occurs entirely at the pore mouth. The concentrations of CO and NO are zero everywhere under these conditions.
Figure 15. Concentration versus Length at 1000°K
Figure 16. Assumed Concentrations versus Length at Temperature > 1000°K
Effect of Pore Length and Pore Radius

This effect is shown in Figures 17, 18, 19 and 20. From Figure 17 it can be seen that the concentration of oxygen at pore end decreases as the radius is decreased and as the length is increased. Figure 18 shows that the concentration of CO decreases as the radius increases and as the length decreases. Figure 19 shows that the flux of NO is increased as the radius is decreased and as the pore length is increased. Figure 20 shows that the flux of CO increases as the radius decreased and so the pore length is decreased.

Effect of $K_3$

Sensitivity of the results of the values of $K_3$ was examined because $K_3$ is the least well known of all the rate constants used. Figure 21 shows the effect of $K_3$ on the flux of NO. From this figure it is shown that the flux of NO increases as the value of $K_3$ is decreased, although the curves have the same qualitative behavior as shown in Figure 19.

Discussion of Pore Model

From Figures 15 and 16 it is concluded that the pore model predicted a very fast reaction at temperatures higher than 1000°K. Thus the reaction takes place at the particle surface and no reaction or diffusion occurs inside the pore. The fact that the concentration of oxygen at pore end decreases with decreasing pore radius and increasing pore length as shown in Figure 17 occurs because a decrease in pore
Figure 17. Concentration of O₂ at Pore End versus Dimensionless Pore radius
Figure 18. Concentration of CO at Pore End versus Dimensionless Pore Radius

$T = 1000^\circ K$
Figure 19. Flux of NO versus Dimensionless Pore Radius
Figure 20. Flux of CO versus Dimensionless Pore Radius
Figure 21. Effect of $K_3$ on Flux NO

$K_3 = 1.09859 \times 10^9 \text{cm}^3/\text{gm mole sec}$

$T = 1000^\circ \text{K}$

$L = 0.05 \text{cm}$
radius or increase in pore length speeds up the surface reaction consuming $O_2$ in comparison to the rate at which $O_2$ can be supplied by diffusion.

The CO concentrations shown in Figure 17 are explained because the CO concentration is tied to the $O_2$ concentration but an analysis of the situation is complicated by the fact high $O_2$ values may or may not lead to high CO values depending on whether the surface reaction producing CO is more dominant than the homogeneous reaction consuming CO. When the surface reaction dominates (large surface to volume ratio) the CO will increase as the $O_2$ increases, while when the homogeneous reaction dominates (low surface to volume ratio) the CO will decrease as the $O_2$ increases. This reasoning explains why the lines in Figure 18 cross, while the lines in Figure 17 do not.

The net flux of NO or CO leaving the pore mouth decreases with increasing pore radius because the surface reactions producing NO and CO are favored over the homogeneous reduction consuming NO and CO by a high surface to volume ratio. The effect of pore length or particle size on the flux of NO and CO is more complex but it appears that a long pore gives the NO and CO more time to be converted to $N_2$ and $CO_2$. It should be noted that NO and CO behave similarly because they are both intermediate products. From Figure 21 it can be concluded that, in fact, the absolute value of the flux of NO is quite sensitive to the value of $K_3$, inasmuch as a high value of $K_3$ will increase the rate of conversion of NO to $N_2$ and decrease the net flux. However Figure 21
shows that the value of $K_3$ does not change the qualitative behavior of the NO flux and so the overall conclusions remain the same and are not sensitive to the actual value of $K_3$ chosen.

For small pore lengths; $L = 0.01$ cm the system is reaction controlled and the concentration of oxygen was roughly constant within the pore. This case resulted in the highest flux of NO. At this small pore length calculation with smaller radii resulted in numerical instabilities. In the case of $O_2$ and CO both diffusion and reaction are equally important when the pore length is greater than 0.01 cm. This is apparent from evaluations of the Thiele parameters $h_{1p}$, $h_{2p}$, shown on Tables 3 and 4, in which for $r/L = 0.1$ the Thiele parameters have an average value close to unity. The large values of $h_{1p}$ (See Tables 3 and 4), which is the Thiele parameter describing the ratio of the homogeneous NO reduction reaction to diffusion, indicate that as far as reduction of NO is concerned the rate is controlled by diffusion of NO along the pore. However, as far as formation of NO at the surface is concerned both reaction and diffusion are important for the whole system. This is in contrast to the work by Fine et al. (1971), in which it was postulated for the combustion of pulverized coal in a fluidized bed that at $1000^\circ K$ chemical kinetics alone are rate controlling.
Table 3. Thiele Parameter for Pore Model $L = 0.10$ cm

<table>
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<tr>
<th>radius</th>
<th>$h_{1p}$</th>
<th>$h_{2p}$</th>
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<th>$h_{4p}$</th>
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Table 4. Thiele Parameter for Pore Model $L = 0.05$ cm

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<td>2.1024</td>
<td>0.0631</td>
<td>3.6529</td>
<td>13.775</td>
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Film Model

Since internal pore size characteristics are not important in typical pulverized coal combustion, it is apparent that here the homogeneous reactions must occur in a stagnant film surrounding the burning char particle. The important results obtained from the film model are the concentration profiles of $O_2$, $CO$ and $NO$, the effect of particle diameter, the effect of $CO$ concentration outside the film, the effect of temperature and the effect of $K_3$ on the percent conversion of fuel nitrogen to NO. In each case the film thickness was determined by that which allowed 95 percent of the $CO$ to be converted in the neighborhood of the char particle and the percent conversion of fuel nitrogen was calculated according to Equation 76.

Effect of Distance

The profiles of $O_2$, $CO$ and $NO$ are shown in Figure 22 where it can be seen that oxygen decreases very rapidly near the particle surface. $CO$ decreases exponentially as the distance from the particle surface increases. $NO$ also decreases as the distance from the particle is increased. The base case for the film model was determined to be the one where the radius of the particle is 0.005 cm or 50 microns, the concentration of $O_2$ at the char environment is 10.5 percent, $CO$ is 95 percent consumed and the temperature is $1000^\circ K$. This corresponds roughly to the combustion of 100µ char particles resulting from pulverized coal combustion at 20 percent overall excess air (see Appendix B).
Figure 22. Concentration Profiles versus Film Distance
Effect of $K_3$

There is indeed an effect of $K_3$ on the percent conversion of fuel nitrogen to NO, as shown in Figure 23. However, since the original value of $K_3$ gave conversions of fuel nitrogen in excess of 99 percent, the value of $K_3$ was adjusted to obtain about a 50 percent conversion of fuel nitrogen to NO because this type of conversion has been reported in the literature (Pershing et al. 1973). Thus the value of fifty times $K_3$ is subsequently used in all results presented in this section. This shows the importance in obtaining rate data which will permit evaluation of a more accurate value for $K_3$.

Effect of Particle Diameter

The effect of particle diameter is shown in Figure 24 where it is apparent that the conversion of fuel nitrogen to NO is reduced as the particle diameter is increased.

Effect of Percent CO Outside the Film

The effect of percent CO outside the film is shown in Figure 25 where it is shown that the percent conversion is reduced as the amount of CO outside the film is increased. In this case the film thickness is fixed at 0.0529 cm because 95 percent conversion of CO within the film does not have physical significance when there is CO outside the film which is not reacting. It is observed that the CO profile goes through a minimum for these cases, because a reaction sink is present in the stagnant film.
Figure 23. Effect of $K_3$ on Percent Conversion of Fuel N to NO

$K_3 = 1.0989E+11 \frac{cc}{gm \ mole \ sec}$
Figure 24. Effect of Diameter of Particle on Percent Conversion Fuel N to NO
Figure 25. Effect of Percent CO in Outside Film on Percent Conversion Fuel N to NO

Figure 26. Effect of Percent O₂ in Char Environment on Percent Conversion Fuel N to NO
Effect of $O_2$ in Char Environment

The effect of $O_2$ in the percent conversion of NO is shown in Figure 26. It can be seen that the percent conversion is decreased as percent $O_2$ increases, provided the particle diameter is kept constant.

Effect of Temperature

The effect of temperature is shown in Figure 27 where a small increase in percent conversion is observed as the temperature is increased.

Effect of Simultaneously Changing Particle Size and Percent $O_2$ Outside Film

This effect was studied to simulate the fate suffered by a burning char particle which is simultaneously decreasing its size while consuming $O_2$ as might occur in pulverized coal combustion. It was assumed that all the carbon was converted to $CO_2$ and that no CO was built up in the gas surrounding the film. The calculation was done in five steps, with 20 percent of the carbon being consumed in each step. At the beginning of each step a mass balance determined the particle size and surrounding stoichiometry, while CHARFCO determined the rate of carbon consumption and thus the time interval between each step. Program CHARFNO then determined the moles/sec of NO emitted, from which the total moles of NO produced would be calculated. Results obtained from this calculation are shown in Table 5, and details of the method are shown in Appendix C. This procedure was repeated for several overall stoichiometries (see Table 5) and resulted in a plot of ppm NO as a
Figure 27. Effect of Temperature on Percent Conversion of Fuel N to NO
Table 5. Calculation of PPM NO\textsubscript{x} as Function of Time

<table>
<thead>
<tr>
<th>Overall Stoich.</th>
<th>Percent O\textsubscript{2}</th>
<th>Moles/sec Carbon Consumed</th>
<th>Moles/sec Carbon Consumed</th>
<th>Time Interval (sec)</th>
<th>Moles/sec NO Produced During Interval</th>
<th>PPM NO \textsubscript{Cumul.} Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>Step Diameter</td>
<td>Film</td>
<td></td>
<td></td>
<td></td>
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function of time as shown in Figure 28. It can be seen that as stoichiometric air decreased the particle time increases. At substoichiometric air ratios the particle does not burn out, because the model assumed that all the carbon must go to CO$_2$ rather than CO. The NO versus time profiles are interesting; the ppm NO increases with excess air, while the converse is true for the resultant ppm NO emitted after particle burnout.

Discussion for Film Model

The shape of the concentration profiles as shown in Figure 22 is explained by the formation of CO and NO at the surface and their homogeneous depletion in the film, while oxygen is consumed at the surface and at the film. It may be deduced from the O$_2$ profile that in the case of oxygen the surface reaction is faster than the homogeneous reaction.

Increasing the order of $K_3$ has the effect of increasing the rate of reduction of NO to N$_2$ and thus reducing the amount of NO produced.

Figure 24 shows that the conversion of fuel nitrogen to NO is reduced as the diameter of the particle increases. Increasing particle diameter increases the rate of the film volume to the particle surface and therefore favors the homogeneous reduction reaction of NO to N$_2$ against the surface reaction forming NO.

The effect of increasing CO concentration outside the film as shown in Figure 25 is significant because it may be conjectured that the effect of lowering excess air is to increase the free stream CO concen-
Cumulative ppm NO (Reduced to Stoichiometric)

Incomplete particle burnout

Figure 28. PPM NO versus Time (Basis no CO in Free Stream)
tation. If this conjecture holds, Figure 25 predicts the observed effect of excess air on fuel nitrogen conversion. However, the physical situation simulated by this model is somewhat of an artifact since all reaction has been constrained to occur only in the stagnant film. This leads to profiles of CO which go through a minimum inside the film, which may not be physically reasonable. Increased levels of CO result throughout the film under these conditions however, and these tend to favor the reduction of NO to N₂, through Reaction IV, Figure 3.

At a constant particle diameter the effect of decreasing O₂ in free stream is to increase fuel nitrogen conversion. If it is conjectured that the effect of excess air is to only lower the O₂ concentration then this result does not agree with observed data (Pershing et al. 1973). However it should be noted that in char combustion both particle diameter and O₂ concentration change simultaneously and so this coupled effect is described below.

The effect of decreasing the O₂ at the free stream is found to decrease all concentrations at the surface and since the formation reactions are first order and the consumption reactions are second order, the balance between formation and destruction is shifted towards formation. If O₂ is decreased and CO is increased the observed dependence of the conversion of fuel nitrogen would be predicted by this model, although this would depend entirely on the relative values of the O₂ and CO in the free stream.
When a char particle burns it consumes $O_2$ and is itself consumed to form (in this model) $CO_2$. Thus it is necessary to complete a stepwise calculation as shown in Table 5 and Figure 28, which takes into account both of these effects. The results, Figure 28, show that particle burnout times have the observed dependence on excess air (Field et al. 1967) and that they are of correct order of magnitude (0.3-1.0 sec). The resulting NO emissions, however, do not follow the observed dependence as excess air, although they do so at any single given time before the particle has had a chance to burn out completely. This anomalous behavior may be due to the fact that decreasing excess air has the additional effect of increasing CO concentration as well as decreasing $O_2$ concentrations. Obviously more furnace data is needed.

The effect of temperature shown in Figure 27 is especially interesting and agrees qualitatively with the observed fact that flue gas recirculation is ineffective as a means of reducing fuel NO. This weak temperature dependence is a result of the role of diffusion and weakly temperature dependent homogeneous reaction, even though the surface reaction has a strong temperature dependence. Calculation of the Thiele parameter, as shown in Table 6, show that, in fact, the system is diffusion controlled, and this leads in general to a weak temperature dependence.
Table 6. Thiele Parameter for Film Model at 2000°K

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<tr>
<th>R</th>
<th>δ</th>
<th>( h_{1f} )</th>
<th>( h_{2f} )</th>
<th>( h_{3f} )</th>
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CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Pore Model

At a particle temperature of above 1000°K, pore size has very little effect on the overall NO formation rate because at high temperatures the reactions take place on the surface of the particle and very little happens inside the pore. At temperatures of 1000°K or below, pore size and length is important. High NO from fuel nitrogen is formed by small short pores. The reason for this is that under these conditions the surface NO formation reaction is favored over the subsequent homogeneous reduction step. At 1000°K diffusion as well as kinetic mechanisms are equally important. This is concluded from the Thiele parameter which can be identified, and which gives an average value very close to unity.

These results mean that under conditions of fluid bed combustion, where temperatures are below 1000°K the pore size characteristics are important in determining the selectivity of the char particles to NO formation. Thus, since char pore size is determined by the treatment undergone by coal prior to carbonization it is apparent that methods used to manufacture the char will affect the NO emissions when that char is burned at low temperature, and that chars of similar fuel nitrogen contents but differing pore characteristics will emit different levels of NOx.
**Film Model**

At temperatures of 2400°C and below particle diameter is important. High NO from fuel nitrogen is produced by small particles. The reason is that there is less CO produced hence less N₂ is formed from NO. High NO can be produced when there is no CO present in the free stream since the increased amount of CO favors the reduction of NO to N₂. As temperature is increased a small monotonic increase is observed. This is in agreement with work by Pershing et al. (1973) where it was postulated that fuel NO does not depend strongly on temperature. This effect has not been theoretically predicted by other workers prior to this work.

This study has shed new light on the effect of excess air on fuel nitrogen conversion. If the effect of excess air is to increase the free stream CO concentration then the results presented here agree with observed data (Pershing et al. 1973). If on the other hand the effect of excess air is to solely decrease the free stream O₂ concentration, then this model predicts an unusual (or rarely observed) inverse dependence on excess air. Obviously more in-furnace data is called for, so that free stream CO and O₂ concentrations can be correlated with overall excess air values.

Another point requiring further clarification is the thickness of the stagnant film around a burning char particle. A stagnant film model is reasonable because, according to Field et al. (1967) the smallest scale of turbulence in a pulverized coal flame is over an order of magnitude greater than the particle diameter. In this work
it was assumed, arbitrarily, that the film thickness was determined by the conversion of CO to CO\textsubscript{2} so that at the outer edge 95 percent of CO had been converted. The problem of NO conversion in this film is thus, one of competition with CO conversion and is quite complex. What is needed is data to show how much CO is converted to CO\textsubscript{2} in the neighborhood of the particle, how much escapes to the free stream, and how this depends on the environment around the particle.

The most uncertain parameter used is the value for K\textsubscript{3}. Hence it is recommended that work should be done to narrow down the actual value of this rate coefficient and to determine the reaction order with respect to CO, H\textsubscript{2}O and NO. In fact, an accurate value of K\textsubscript{3} will help determine just how important the char fuel nitrogen is. For example if the value of K\textsubscript{3} is found to be very large it would appear that the char fuel nitrogen can all be converted to N\textsubscript{2} and that from a practical point of view it is desirable to modify combustion conditions in the coal volatilization regime so that a larger percentage of the nitrogen is carried into the char. This can be done by adjusting the heating rate of the coal, close to the burner.

Since several numerical instabilities were found it is recommended to use an integration algorithm which will allow the solution of stiff differential equations. Because this study was based only on global reaction it is recommended to analyze the two models using elementary reactions. The effect of pore as well as the film should be studied simultaneously. Since in this project no consideration was given to the fact that the particle is being consumed continuously it
is also necessary to incorporate this aspect if a more realistic model is to be obtained. A stepwise procedure, as used in this work, is only quite approximate. A simulation should be developed so that more complex kinetic mechanisms and heat transfer can be taken into account. In addition the model should be extended from single particles to swarm or clouds of burning char particles, in order to simulate combustion generated air pollution from pulverized coal furnaces.
APPENDIX A

PROGRAM CHARFNO AND SET OF RESULTS
PROGRAM CHARFNO(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)

C THIS PROGRAM SOLVES A SYSTEM OF SIX FIRST ORDER, NON LINEAR DIFF.
C EQUATIONS THAT DESCRIBE THE FORMATION OF NO AND CO, AND THE DEPLE-
C TION OF OXYGEN IN THE FILM SURROUNDING A BURNING CHAR PARTICLE.

C***********************************************************************
C NOTE **********************************************************************
C***********************************************************************

C THIS PROGRAM USES THE RESULTS FROM PROGRAM CHARFCO

C***********************************************************************
C A FOURTH ORDER RUNGE-KUTTA-GILL METHOD IS USED. SINCE THE PROBLEM
C IS A BOUNDARY VALUE SYSTEM, THE SEARCH PATTERN METHOD OF HOOKE-
C JEEVES IS USED TO OPTIMIZE A RESIDUAL FUNCTION FOR THE INITIAL
C CONCENTRATION OF NO.

C NOTE
C TWO SEARCH ARE PERFORMED. THE FIRST IS DONE IN ORDER TO DETERMINE
C THE INITIAL CONCENTRATION OF NO TO PREVENT INSTABILITIES.
C WHEN THIS VALUE IS DETERMINED THE REFINED SEARCH PATTERN METHOD
C IS USED.

C PROGRAM CHARFNO IS THE MAIN LINE. IS USED TO READ, CHANGE THE
C VALUE OF THE INITIAL CONCENTRATION OF NO AND CALCULATE THE FLUXES
C AND PERCENT CONVERSIONS.

C THE FOLLOWING SUBROUTINES ARE USED.

C OBJFN - USED TO DEFINE AND CALCULATE THE RESIDUAL FUNCTION TO
C BE MINIMIZED.
C R<GS - USED TO SOLVE THE DIFFERENTIAL EQUATIONS BY THE RUNGE-
C KUTTA-GILL FOURTH ORDER METHOD.
C FCIN - USED TO DEFINE THE DIFFERENTIAL EQUATIONS TO BE SOLVED.
C INITIAL - USED TO CALCULATE ALL THE VARIABLES THAT ARE TO BE USED
C DURING THE RUNNING OF THIS PROGRAM, WHICH DO NOT CHANGE
C WITH THE INTEGRATION.
C PRNOUT - SUBROUTINE USED TO PRINT OUT IN CASE OF DEBUGGING.
C FSOPTNO - SUBROUTINE USED TO FIND IF INSTABILITIES OCCUR WITH THE
C INITIAL GUESS USED FOR NO.
C CHANGE - USED TO REDUCE THE VALUE OF THE INITIAL GUESS FOR NO IF
C INSTABILITIES DO OCCUR.
C CHANGE2 - USED TO INCREASE THE VALUE OF THE INITIAL GUESS FOR NO
C IF CHANGE IS NOT SUCCESSFUL.
C SUPFIN - USED TO DO THE NECESSARY CALCULATIONS TO CHANGE THE STEPS
C FROM TEN TO ONE HUNDRED.
C NEWPRT - USED TO PRINT OUT THE SOLUTION OF THE SYSTEM OF EQUATIONS
C WHEN DEBUGGING IS REQUIRED.

C THE FOLLOWING ENTRIES ARE USED.

C SMCUT - ENTRY IN FSOPTNO DOES THE SAME OPERATIONS AS FSOPTNO,
C BUT FOR ONE HUNDRED STEPS.
C PRTSTOP - ENTRY IN NEWPRT. IT DOES PRINTS THE FINAL INTEGRATION
C STEPS WHEN THE INDEX HAS EXCEEDED 1011.
THE FOLLOWING VARIABLES ARE USED IN THIS PROGRAM.

A  ARRAY FOR THE INITIAL GUESS.
AL3  VALUE WHERE NUMERICAL INSTABILITIES OCCUR.
A4FNN  FINAL MOLE FRACTIONS, WHERE NN IS CO, NO, AND O2 RESPECTIVELY.
A4FINN  INITIAL MOLE FRACTIONS, WHERE NN IS CO, NO, AND O2 RESPECTIVELY.
CD  ARRAY FOR COEFFICIENTS USED TO CALCULATE THE DIFFUSIVITIES.
CVO  CONCENTRATION OF NO.
CONI-6  VALUES THAT REMAIN CONSTANT THROUGHOUT THE INTEGRATION.
CONV1-3  CONVERSION OF O2, CO AND NO, RESPECTIVELY.
CUT  VALUE USED TO REDUCE THE VALUE OF DEL.
C1  INITIAL CONCENTRATION OF O2, SUPPLIED BY CHARFCO.
C2  INITIAL CONCENTRATION OF CO, SUPPLIED BY CHARFCO.
DEL  ARRAY FOR THE VALUES USED TO CHANGE THE INITIAL GUESS.
DF  DIAMETER OF FILM.
DFLTAX  INCREMENTS OF THE INDEPENDENT VARIABLE FOR THE INTEGRATION.
DI  DIAMETER OF PARTICLE.
D1  DIFFUSIVITY OF O2 IN NITROGEN.
D2  DIFFUSIVITY OF CO IN NITROGEN.
D3  DIFFUSIVITY OF NO IN NITROGEN.
EPS  ARRAY TO STORE THE TOLERANCE FOR THE RESIDUAL FUNCTION.
FLAG  LOGICAL USED TO PRINT OUT THE RESULTS OF THE INTEGRATION.
IS  SET TO 1.
FLWINN  INITIAL FLOW, WHERE NN IS CO, NO, AND O2 RESPECTIVELY.
FLXONN  FINAL FLOW, WHERE NN IS CO, NO, AND O2 RESPECTIVELY.
FLXI1-3  INITIAL FLUX FOR O2, CO, AND NO RESPECTIVELY.
FLEXONN  FINAL FLUX FOR O2, CO, AND NO RESPECTIVELY.
INDEX  VALUE USED TO ACTIVATE DEBUGGING PRINTOUT WHEN SET TO 1.
JSTEP  THE NUMBER OF STEPS BEING USED, EITHER 10 OR 100.
K1-4  REAL, RATE COEFFICIENT FOR THE CHEMICAL REACTIONS.
LIM  REAL, LOWER LIMIT FOR THE CONCENTRATIONS.
MAYNE  COUNTER TO DETERMINE IF AN ACCEPTABLE SOLUTION HAS BEEN OBTAINED.
NE  NUMBER OF EQUATIONS.
NFOP  COUNTER USED TO DETERMINE THE NUMBER OF TIMES THAT FSOPT HAS BEEN CALLED.
NVTOP  NUMBER OF VARIABLES TO BE OPTIMIZED.
P  PRESSURE.
RES  RESIDUAL FUNCTION TO BE MINIMIZED, DEFINED IN OBJFN.
RF  RADIUS OF FILM.
RHO  MOLAR DENSITY.
ULCI-3  MAXIMUM ALLOWABLE CONCENTRATION OF O2, CO AND NO RESPECTIVELY.
RI  PARTICLE RADIUS.
T  TEMPERATURE.
VECT  ARRAY USED TO INCREASE THE CHANGE IN THE VARIABLE THAT IS BEING OPTIMIZED IF THE MOVES ARE SUCCESSFUL.
X  ARRAY TO STORE THE VALUES THAT ARE TO BE OPTIMIZED.
XX  VALUE THAT IS CURRENTLY BEING OPTIMIZED.
Y  VALUE THAT IS BEING OPTIMIZED FOR NO.
YBASE  BASE POINT OBTAINED IN THE OPTIMIZATION.
Y2RP  IMPROVED VALUE OF YBASE OBTAINED IN THE OPTIMIZATION.
YFINAL  ARRAY THAT STORES THE FINAL VALUES OBTAINED IN THE INTEGRATION.
YINIT  ARRAY TO STORE THE INITIAL VALUES USED IN THE INTEGRATION.
VALUE USED TO DETERMINE IF THERE IS AN IMPROVEMENT IN THE OPTIMIZATION.

READING SEQUENCE

CARD NUMBER 1

| COL. 1 - 5 | NVTOP, THE NUMBER OF VARIABLES TO BE OPTIMIZED |
| COL. 6 - 10 | N, THE NUMBER OF DIFFERENTIAL EQUATIONS PLUS ONE |
| COL. 11 - 15 | LLIM, THE LOWER LIMIT FOR THE CONCENTRATIONS, USUALLY 0.0, F5.0 FORMAT |
| COL. 16 - 20 | T, TEMPERATURE, DEG. K, F5.0 FORMAT |
| COL. 21 - 25 | P, PRESSURE, ATM., F5.0 FORMAT |
| COL. 26 - 35 | RL, RADIUS OF THE CHAR PARTICLE, CM, F10.0 FORMAT |
| COL. 36 - 45 | RF, RADIUS OF THE FILM SURROUNDING THE PARTICLE, CM, F10.0 FORMAT |

CARD NUMBER 2

| COL. 1 - 5 | IERR, DEBUGGING PARAMETER, 1 FOR EXTENSIVE PRINTOUT |
| COL. 6 - 10 | 0 FOR REGULAR PRINTOUT |
| COL. 11 - 15 | C1, THE CALCULATED INITIAL VALUE OF OXYGEN FROM CHARFCO, E13.0 FORMAT |
| COL. 16 - 31 | C2, THE CALCULATED INITIAL VALUE OF CO FROM CHARFCO, E13.0 FORMAT |

****** NOTE ******************** **********************************
* CARD NUMBER 2 IS PUNCHED BY CHARFCO. *

CARD NUMBER 3

| COL. 1 - 13 | CD, DIFFUSION COEFFICIENT AS A FUNCTION OF TEMP. E13.0 FORMAT |
| COL. 14 - 27 | EPS, THF TOLERANCE FOR THE RESIDUAL FUNCTION E13.0 FORMAT |
| COL. 28 - 41 | DEL, THE INCREMENT OR DECREMENT TO BE ADDED OR SUBTRACTED FROM THE INITIAL GUESS. E13.0 FORMAT |

NOTE IF THE SUPPLIED VALUE FOR DEL IS TOO LARGE, IS REDUCED BY THE PROGRAM.

THIS CARD SHOULD BE REPEATED FOR EVERY VARIABLE THAT IS TO BE OPTIMIZED.

CARD NUMBER 4

| COL. 1 - 13 | CON1, E13.0 FORMAT |
| COL. 14 - 26 | CON2, E13.0 FORMAT |
| COL. 27 - 39 | CON3, E13.0 FORMAT |
| COL. 40 - 52 | CON4, E13.0 FORMAT |
| COL. 53 - 65 | ULS1, E13.0 FORMAT |
| COL. 66 - 78 | ULS2, E13.0 FORMAT |
NOTE  THIS CARD IS PUNCH BY CHARFCO.

CARD NUMBER 5

THIS CARD IS READ BY A NAMELIST.
SEE EXAMPLE BELOW

CARD NUMBER 5
THI S CARD IS READ BY A NAMELIST.
SEE EXAMPLE BELOW

CARD NUMBER 5
THI S CARD WILL BE PUNCHED OUT IF THE VALUE OF ITEM P IS SET
EQUAL TO 1 IN PROGRAM CHARFCO.

LOGICAL FLAG
REAL <1,K2,K3,K4,LLIM

COMMON /DS/ DELTAX,IERR,LLIM,N,NVTOP,RI,RF,RHO,X(5)
COMMON /SET2/ CON1,CON2,CON3,CON4,CON5,CON6
COMMON /SET3/ ISTEP,YCRP,YBASE,YPTN
COMMON /ERR/ AL3,INDEX
COMMON /RCOEF/ K1,K2,K3
COMMON /SAV/ SAV
COMMON /DIFF/ D3

DIMENSION A(5),CD(5),EPS(5),DEL(5),VECT(5),YINIT(10),YFINAL(10)

NAMELIST /RATE/ K1,K4,D1,D2

*** READ INPUT PARAMETERS ***

51 READ(5,100) NVTOP,N,LLIM,T,P,RI,RF
IF(EOF(5)) 999,52
52 READ(5,101) IERR,C1,C2
READ(5,105) (CD(I),EPS(I),DEL(I),I=1,NVTOP)
READ(5,110) CON1,CON2,CON3,CON4,ULC1,ULC2
READ(5,110) RATE

ICK=0
FLAG=.F.
YCRP=YBASE=YPTN=0.0
ISTEP=10
NF=N+1
NE=N-1
DELTAX = (RF-RI)/10.0

CALL INITIAL TO EVALUATE THE PARAMETERS
CALL INITIAL (A,CD,C1,DEL,D3,P,RHO,T,ULC3)

X(1)=C1
BEGIN FAST OPTIMIZATION
CALL SOPTNO(DEL,DELTAX,IC,IERR,N,NFOP,R1,RF,RHO,X,Y)

IF(IC.GT.3) GO TO 55
AL3=0.0

OUTPUT FOR CALCULATED VALUES AND PARAMETERS THAT WERE READ IN.
WRITE(6,200) NVTOP,K1,NE,K2,DELTAX,K3,RF,K4,RI,01,P,02,T,03
WRITE(6,210) (A(I),EPS(I),DEL(I),I=1,NVTOP)
WRITE(6,225) CON1,LLIM,CON2,ULC1,CON3,ULC2,CON4,ULC3,CON5,RHO,CON6

BEGIN METHOD OF HOOKES AND JEEVES
12 CONTINUE
DO 4 I=1,NVTOP
  4 A(I)=Y
INDEX=0
DO 5 L = 1,NVTOP
  5 Y = A(L)
  5 YVEC(L)=0.0
  5 CONTINUE

XX=Y
LL=1

CALL OBJFN(XX,LL,RES)
YBASE=RES
CUT=1.000000

WRITE THE VALUES AT THE INITIAL BASE POINT
WRITE(6,300) Y
WRITE(6,305) YBASE

VARY EACH VARIABLE IN AN ATTEMPT TO FIND A BETTER LOCATION
10 YCRP=YBASE
15 DO 20 I = 1,NVTOP
    20 LL=I
C TAKE EXPLORATORY STEPS ABOUT THE BASE POINT

XX = A(I) + (CUT*DEL(I))
CALL OBJFN(xx,LL,RES)
IF(RES,LT,YCRP) GOTO 45
XX = A(I) - (CUT*DEL(I))
CALL OBJFN(xx,LL,RES)
IF(RES,GE,YCRP) GOTO 40

45 YCRP=RES
CNO=53L
DEL(I)=DEL(I)*1.5
35 VECT(I) = VECT(I) + (XX-A(I))
Y=XX
GOTO 20

40 Y = A(I)
DEL(I)=DEL(I)/2.0
20 CONTINUE

C IF EXPLORATORY MOVES ARE UNSUCCESSFUL, CUT THE STEP SIZE, SEE IF
C YOU ARE WITHIN TOLERANCE, AND MAKE MORE EXPLORATORY STEPS IF
C YOU ARE NOT.

IF(YCRP,LT,YBASE) GOTO 50
MAYBE=0
DO 50 I = 1,NVTOP
C4K=CUT*DEL(I)*2.0
IF(CHK,LE,EPS(I)) MAYBE=MAYBE+1
56 CONTINUE
IF(MAYBE,LT,NVTOP) 15,60
50 YBASE=YCRP

C IF EXPLORATORY MOVES ARE SUCCESSFUL, TRY A PATTERN SEARCH

74 DO 62 I=1,NVTOP
A(I) = Y
Y=Y+VECT(I)
62 CONTINUE
LL=1
XX=Y
CALL OBJFN(xx,LL,RES)
YPIN=RES
IF(YPIN,LT,YJASE) 64,66
66 DO 92 J=1,NVTOP
Y = A(J)
82 VECT(J)=Y
GOTO 10
64 YJASE=YPIN
YCRP=YPIN
IF(RES,GT,1.0E-06) GO TO 80
CVO = SOL
91 CONTINUE
DO 30 I=1,NVTOP
VECT(I)=VECT(I)*2.0
97 A(I) = Y
GO TO 74
60 CONTINUE
WRITE VALUES FOR RES AND C3 IF THEY ARE SATISFACTORY

WRITE(6,345) ISTEP,AL3
WRITE(6,330) INDEX
WRITE(5,335) CNO
WRITE(6,340) YCRP

ICK=ICK+1
IF(IERR.EQ.0) CALL NEWPRT(C1,C2,CON3,CON4,CON5,D3,DELTA,N,RI,RF)
IF(ICK.GT.1) GOTO 16

CHECK FOR STEPS

IF(IERR.EQ.1) CALL SUPFIN(DEL,DELTA,ISTEP,CNO)
CALL SMOUT(DEL,DELTA,IC,IERR,N,NVTOP,RI,RF,RHO,X,CNO)

START METHOD OF HOOKES JEEVES WITH 100 STEPS

50 TO 12
15 CONTINUE

INITIALIZE VALUES FOR THE INTEGRATION

YINIT(1) = RI
YINIT(2) = X(1)
YINIT(3) = CON3*X(1)
YINIT(4) = X(2)
YINIT(5) = CON4*X(1)
YINIT(6) = CNO
YINIT(7) = CON5*X(1)
YINIT(8) = -03*YINIT(7)
WRITE(6,230) (YINIT(I),I=1,NF)

SET FLAG = .TRUE. TO PRINT THE VALUES OF THE INTEGRATION

FLAG = .T.
CALL RKG5(YINIT,YFINAL,RF,N,DELTA,FLAG)
FLAG = .F.

CALCULATE CONVERSIONS

FLXI1 = -CON3*C1*D1
FLX01 = -01*YFINAL(3)
FLXI2 = -CON4*C1*D2
FLX02 = -02*YFINAL(5)
FLXI3 = -CON5*C1*D3
FLX03 = -03*YFINAL(7)
CONV1 = (FLXI1*RI*RI)/(FLXO1*RF*RF)
CONV2 = (FLX12*RI*RI)/(FLXO2*RF*RF)
CONV3 = (FLXI3*RI*RI)/(FLXO3*RF*RF)

RCONV1 = ((1./CONV1)-1.)*100.
RCONV2 = ((1./CONV2)-1.)*100.
RCONV3 = ((1./CONV3)-1.)*100.

AMFI02 = C1/RHO
AMFFJ2 = YFINAL(2)/RHO
AMFC01 = C2/RHO
AMFFNO = YFINAL(4)/RHO
AMFINO = CN0/RHO

DI = 2.*RI
DF = 2.*RF
PT = 3.1416
DI2P = DI*DI*PI
DF2P = DF*DF*PI

FLW102 = DI2P*FLXI1
FLWJ02 = DF2P*FLXO1
FLWICO = DI2P*FLXI2
FLWICO = DF2P*FLXO2
FLWINO = DI2P*FLXI3
FLWONO = DF2P*FLXO3

WRITE (5,360) FLXI1,FLXO1,RCONV1,FLXI2,FLXO2,RCONV2,FLXI3,FLXO3,
RCONV3,AMFI02,AMFFJ2,DI,AMFC01,AMFFNO,AMFINO,FLW102,
FLWJ02,FLWICO,FLWICO,FLWINO,FLWONO
GO TO 51
55 WRITE (6,350)

C **** FORMATS FOR INPUT ****

101 FORMAT (2I5,3F5.0,2F10.0)
104 FORMAT (3E13.0)
110 FORMAT (6E13.0)

C **** FORMATS FOR OUTPUT ****

200 FORMAT (IH1,T20,*NUM OF VAR TO BE OPT. =*,I5,T79,*K1 =*,1PE13.6,/, 
1T20,*NUM OF DIF. EQUATIONS =*,I5,T79,*K2 =*,E13.6,/,T36,*DELTAX = 
2*,E13.6,T79,*K3 =*,E13.6,/,T31,*OUTER SHELL =*,E13.6,T79,*K4 =*, 
3E13.6,/,T31,*INNER SHELL =*,E13.6,T79,*O1 =*,E13.6,/,T34,*PRESSURE 
4 =*,E13.6,T79,*O2 =*,E13.6,/,T31,*TEMPERATURE =*,E13.6,T79,*O3 =*, 
5E13.6,/////)
GO TO 51
903 CALL EXIT
END
SUBROUTINE OBJFN(XX, LL, RES)

C THIS SUBROUTINE IS USED TO EVALUATE THE RESIDUAL FUNCTION
C IT CALLS PRTOUT, PRTSTOP AND RKGS.

REAL LLIM
LOGICAL FLAG

COMMON /OS/ DELTAX, IERR, LLIM, N, NVTOP, RI, RF, RHO, X(5)
COMMON /SET2/ CON1, CON2, CON3, CON4, CON5, CON6
COMMON /ERR/ AL3, INDEX
COMMON /SAV/ SOL
COMMON /NEW/ YINIT
COMMON /NU1/ C3, C3F, AC, RSS

DIMENSION YINIT(10), YFINAL(10)

AL3 = 0.0

C INITIALIZE VALUES FOR THE INTEGRATION

YINIT(1) = RI
YINIT(2) = X(1)
YINIT(3) = CON3*X(1)
YINIT(4) = X(2)
YINIT(5) = CON4*X(1)
YINIT(6) = XX
YINIT(7) = CON5*X(1)
INDEX = INDEX + 1
C3 = XX
SOL = YINIT(5)

C CHECK IF THE NEW VALUE IS WITHIN BOUNDS.

IF(XX.LT.LLIM.OR.XX.GT.RHO) GO TO 16
IF(INDEX.EQ.100U) IERR = 1
IF(INDEX.EQ.1011) CALL PRTSTOP(C1, C2, CON3, CON4, CON5, D3, DELTAX, N, RI
1., RF)
FLAG = .F.
CALL RKGS(YINIT, YFINAL, RF, N, DELTAX, FLAG)

C CHECK FOR AL3

IF(YFINAL(6).NE.0.0) GO TO 20
GO TO 15

C CONVERT FINAL VALUES TO MOLE FRACTIONS

20 AC = YFINAL(6)/RHO

C CALCULATE RESIDUAL FUNCTION

RES = AC*AC
RSS = RES

IF(IERR.EQ.1) CALL PRNTOUT
RETURN
15 CONTINUE

C3F = YFINAL(6)

C CALCULATE THE RESIDUAL FUNCTION

RFS = 1.0E+100
AC=0.0
PSS=RES
IF(IERR.EQ.1) CALL PRNOUT
AL3=0.
RETURN

C CALCULATE THE RESIDUAL FUNCTION

16 RES = 1.0E+100
RETURN

END
SUBROUTINE RKGS(YINIT,YFINAL,XFINAL,N,DELTAX,FLAG)
C
C THIS SUBROUTINE USES THE FOURTH ORDER RUNGE-KUTTA-GILL METHOD
C TO SOLVE THE DIFFERENTIAL EQUATIONS DEFINED IN FCTN.
C IT CALLS FCTN.

LOGICAL FLAG

COMMON /ERR/ AL3, INDEX
COMMON /ERT/ Y(I0,5), AK(I0,5)
COMMON /DIFFI/ D3

DIMENSION A(4), B(4), C(4), YINIT(10), YFINAL(10), Q(10,5)
DIMENSION YPRNT(10)

AL3=0.0
M=9+N
MIS=0

C SET THE CONSTANTS TO BE USED IN THIS METHOD.

A(1) = 0.5
A(2) = 0.292693219635
A(3) = 1.707106781365
A(4) = 1./6.
B(1) = 2./3.
B(2) = 1.
B(3) = 1./3.
B(4) = 2./3.
C(1) = A(1)
C(2) = A(2)
C(3) = A(3)
C(4) = A(1)
DO 1 I = 1, N
Y(I,1) = YINIT(I)
1 2(I,5) = 0.
3 H = DELTAX
4 DO 4 I = 1, N
5 DO 6 J = 2, 5
6 CALL FCTN(J-1)
4 7 DO 8 I = 1, N
8 D = A(J-1)*AK(I,J-1) - B(J-1)*Q(I,J-1)
Y(I,J) = Y(I,J-1) + D*
6 3(I,J) = Q(I,J-1) + 3.*7 -C(J-1)*AK(I,J-1)

C STORE THE NEW VALUE

7 Y(I,1) = Y(I,5)

C CHECK IF THE CRITERIA FOR STABILITY IS MET. IF NOT RETURN
C TO CALLING PROGRAM, OTHERWISE CONTINUE.

IF(Y(I,1),LT,0.0) AL3=XFINAL-Y(I,1)
IF(AL3,LT,1.0E-10) AL3=0.0
IF(AL3,NE.,0.0) GO TO 25
GO TO 27
25 DO 23 I=2,N
23 Y(I,1)=0.0
Y(I,1)=XFINAL
GO TO 35
27 CONTINUE
C PRINT RESULTS IF FLAG IS .TRUE.

IF(FLAG) 50,35
50 CONTINUE
DO 19 I=1,N
18 YPRNT(I)=Y(I,1)
YPRNT(I)=0.3*Y(I,1)
IF(MIS.EQ.1) GO TO 8
WRITE(6,240) (YPRNT(I),I=1,M)
35 CONTINUE
IF(MIS.EQ.1) GO TO 8
DIF=XFINAL-Y(I,1)
C CHECK IF THE FINAL POINT HAS BEEN CALCULATED.

IF(DIF.LT.DELTAX) 70,3
70 MIS=1
M=DIF
IF(Y(I,1).GT.XFINAL) GO TO 8
GO TO 3
8 DO 9 I=1,N
9 YFINAL(I)=Y(I,1)
240 FORMAT(6X,8(2X,1PE13.6)/)
RETURN
END
SUBROUTINE FCTN(JJ)

C THIS SUBROUTINE DEFINES THE DIFFERENTIAL EQUATIONS TO BE SOLVED.
C
C THE FIRST VALUE OF YP IS USED TO DEFINE THE INDEPENDENT VARIABLE

COMMON /SET2/ CON1,CON2,CON3,CON4,CON5,CON6
COMMON /FR1/ Y(10,5),YP(10,5)

YP(1, JJ) = 1.0
YP(2, JJ) = Y(3, JJ)
YP(3, JJ) = CON1*Y(4, JJ)*SQR(Y(2, JJ)) - (2.*Y(3, JJ)/Y(1, JJ))
YP(4, JJ) = Y(5, JJ)
YP(5, JJ) = CON2*Y(4, JJ)*SQR(Y(2, JJ)) - (2.*Y(5, JJ)/Y(1, JJ))
YP(5, JJ) = Y(7, JJ)
YP(7, JJ) = CON6*Y(4, JJ)*Y(6, JJ) - (2.*Y(7, JJ)/Y(1, JJ))

RETURN
END
SUBROUTINE INITIAL(A,CO,C1,DEL,D3,P,RHO,T,ULC3)

C THIS SUBROUTINE EVALUATES THE PARAMETERS THAT ARE NOT CHANGED
C BY THE INTEGRATION.

REAL K1,K2,K3
COMMON /SET2/ CON1,CON2,CON3,CON4,CON5,CON6
COMMON /ROOF/ K1,K2,K3

DIMENSION A(5),CO(5),DEL(5)

RHO=P/(T^82.06)

K2=K1^9.57142571E-03
K3=(1.33875426E+04)/RHO
K3=50.*K3

T15=T^1.5

D3=CO(1)*T15

CON3 = -K2/D3
CON5 = K3/D3

ULC3 = RHO
A(1) = C1

IF(A(1) .LE. DEL(1)) DEL(1) = 0.01*A(1)

RETURN
END
SUBROUTINE PRNTOUT

C THIS SUBROUTINE PRINTS OUT EXTENSIVE INFORMATION IF DEBUGGING IS REQUIRED.

COMMON /SET3/ ISTEP, YCRP, YBASE, YPTN
COMMON /NU1/ C3, C3F, AC, RSS
COMMON /ERR/ AL3, INDEX

WRITE(6,200) INDEX, ISTEP, C3, C3F, AL3, AC, RSS, 1YCRP, YBASE, YPTN


RETURN
END
SUBROUTINE FSOPTEO(DEL, DELTA, IC, IERR, N, NFOP, RI, RF, RHO, X, Y)

C THIS SUBROUTINE DETERMINES IF A13 IS 0.0 IF NOT THEN CALLS
C CHANGE TO CHANGE THE VALUE OF THE INITIAL GUESS UNTIL A13
C IS ZERO.
C IT HAS AN ENTRY, SMCUT THAT DOES THE SAME OPERATION BUT FOR
C 100 STEPS.
C IT CALLS CHANGE AND RKG5.

LOGICAL FLAG

COMMON /SET2/ CON1, CON2, CON3, CON4, CON5, CON6
COMMON /ERR/ A13, INDEX

DIMENSION YINIT(10), YFINAL(10), DEL(5), X(5), SYINIT(10)

C INITIALIZE VALUES FOR THE INTEGRATION

15 YINIT(1) = RI
   YINIT(3) = X(1)
   YINIT(5) = CON3*X(1)
   YINIT(4) = X(2)
   YINIT(5) = CON4*X(1)
   YINIT(6) = Y
   YINIT(7) = CON5*X(1)
   IF(IEERR.GT.3) GO TO 25
   IF(IEERR.EQ.1) WRITE(6,240) (YINIT(I), I=1,N)
   IF(IEERR.EQ.1) FLAG = .T.
   CALL RKG5(YINIT, YFINAL, RF, N, DELTA, FLAG)
   IF(A13.NE.0) GO TO 20
   GO TO 25
20 CALL CHANGE(DEL, IC, NFOP, RHO, Y)
   GO TO 15
25 CONTINUE
RETURN

ENTRY SMCUT

C INITIALIZE VALUES FOR THE INTEGRATION

YINIT(1) = RI
YINIT(2) = X(1)
YINIT(3) = CON3*X(1)
YINIT(4) = X(2)
YINIT(5) = CON4*X(1)
YINIT(6) = Y
YINIT(7) = CON5*X(1)
IF(IEERR.EQ.1) WRITE(6,240) (YINIT(I), I=1,N)
DO 7 J= 1, N
7 SYINIT(J) = YINIT(J)
40 CONTINUE
DO 8 I=1, N
8 YINIT(J) = SYINIT(J)
YINIT(6) = Y
IF (IERR EQ 1) FLAG = .T.
CALL RKG5(YINIT,YFINAL,RF,N,DELTAX,FLAG)
IF (AL3.NE.0.0) GO TO 30
GO TO 35
C IF AL3 NOT ZERO INCREASE THE INITIAL GUESS BY 1.01
30 Y = Y * 1.01
GO TO 40
35 CONTINUE
240 FORMAT (6X,7(2X,1PE13.6))
RETURN
END
SUBROUTINE CHANGE(DEL, IC, NFOP, RHO, Y)

C THIS SUBROUTINES CHANGES THE VALUE OF THE INITIAL GUESS FOR
C THE CASE WHEN TEN STEPS ARE USED.
C TO REDUCE THE VALUE OF AL3.
C IT CALLS CHANGE2 IF AFTER 15 CHANGES THERE IS NO IMPROVEMENT

DIMENSION DEL(5)

IF (NFOP.GT.15) GO TO 30
NFOP=NFOP+1
Y=Y/10.,0
IF (DEL(1).GE.Y) DEL(1)=DEL(1)/10.
10 CONTINUE
RETURN
30 IC=IC+1
CALL CHANGE2(DEL, IC, RHO, Y)
GO TO 10
END
SUBROUTINE CHANUE2(DEL, IC, RHO, Y)

C THIS SUBROUTINE IS USED TO INCREASE THE VALUE OF THE INITIAL GUESS
C BACK TO THE INITIAL VALUE THAT HAD WHEN CHANGE WAS CALLED FOR
C THE FIRST TIME AND THEN INCREASE IT BY 100.

DIMENSION DEL(5)

IF (IC.GT.3) GO TO 10
NN=NFOP
NFOP=0
Y=Y*(10.**NN)*(10.**IC)*100.
IF (Y.GE.DEL(1)) DEL(1)=Y/10.
10 IF (Y.GT.RHO) IC = 30
RETURN
END
SUBROUTINE SUPFIN(DEL, DELTAX, ISTEP, CNO)

C THIS SUBROUTINE CHANGES THE STEPS FROM 10 TO 100 AND CHECKS IF DEL IS LESS THAN CNO.
C
DIMENSION DEL(5)
IF(DEL(1) .GE. CNO)  DEL(1) = CNO/10.0
DELTAX=DELTAX/10.0
ISTEP=100
RETURN
END
SUBROUTINE SUPFIN(DEL, DELTAX, ISTEP, CNO)

C     THIS SUBROUTINE CHANGES THE STEPS FROM 10 TO 100 AND CHECKS
C     IF DEL IS LESS THAN CNO.

DIMENSION DEL(5)
IF(DEL(1) .GE. CNO)  DEL(1) = CNO/10.0
DELTAX=DELTAX/10.0
ISTEP=100
RETURN
END
SUBROUTINE NEWPRT(C1, C2, CON3, CON4, CON5, DELTAX, N, RI, RF)

THIS SUBROUTINE PRINTS THE VALUES OBTAINED FROM THE INTEGRATION
IN CASE OF DEBUGGING.
IT HAS AN ENTRY, PRISTOP THAT PRINT THE LAST INTEGRATION IF THE
INDEX HAS EXCEEDED THE VALUE OF 1011, AND STOPS THE PROGRAM.

LOGICAL FLAG

COMMON /NEW/ YINIT
COMMON /SAV/ SOL

DIMENSION YINIT(10), YFINAL(10)
NF=N+1

INITIALIZE VALUES FOR THE INTEGRATION

YINIT(1) = RI
YINIT(2) = C1
YINIT(3) = CON3*C1
YINIT(4) = C2
YINIT(5) = CON4*C1
YINIT(6) = SOL
YINIT(7) = CON5*C1
YINIT(8) = -03*YINIT(7)
WRITE(6,230) (YINIT(I), I=1,NF)
FLAG = .T.
CALL RKGS(YINIT, YFINAL, RF, N, DELTAX, FLAG)
FLAG = .F.
RETURN

ENTRY PRISTOP

WRITE(6,230) (YINIT(I), I=1,NF)
FLAG = .T.
CALL RKGS(YINIT, YFINAL, RF, N, DELTAX, FLAG)
FLAG = .F.
STOP 777
END
NUMB OF VAR TO BE OPT. = 1
NUMB OF DIF. EQUATIONS = 6
DELTA = 4.790000E-03
OUTER SHELL = 5.290000E-02
INNER SHELL = 5.000000E-03
PRESSURE = 1.000000E+00
TEMPERATURE = 2.000000E+03

K1 = 1.730611E+04
K2 = 1.483381E+02
K3 = 1.096590E+11
K4 = 5.323445E+07
D1 = 3.355804E+00
D2 = 3.531710E+00
D3 = 3.462513E+00

4.157957E-08 1.000000E-12 4.157957E-10

CON1 = 7.931698E+06
CON2 = 1.507328E+07
CON3 = 2.578534E+03
CON4 = -4.900208E+03
CON5 = -4.284116E+01
CON6 = 3.172812E+10

LLIM = 0.
ULC1 = 6.397758E-07
ULC2 = 0.
ULC3 = 6.093103E-06
RHO = 6.093103E-06

THE BASE POINT IS LOCATED AT
C3 = 4.157957E-08

THE RESIDUAL FUNCTION AT THESE POINTS IS: RES = 2.447842E-04

THE NUMBER OF STEPS FOR THE INTEGRATION = 10

AFTER 60 FUNCTION EVALUATIONS

THE OPTIMAL VALUE OF C3 = 5.474524E-09

THE OPTIMAL VALUE OF THE RESIDUAL FUNCTION IS: RES = 2.72314E-13

THE BASE POINT IS LOCATED AT
C3 = 6.107753E-09

THE RESIDUAL FUNCTION AT THESE POINTS IS: RES = 7.009059E-12

THE NUMBER OF STEPS FOR THE INTEGRATION = 100

AL3 = 0.
AFTER 14 FUNCTION EVALUATIONS

THE OPTIMAL VALUE OF C3 = 6.099514E-09

THE OPTIMAL VALUE OF THE RESIDUAL FUNCTION IS 9.97477E-15
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APPENDIX B

CALCULATIONS FOR PERCENT OXYGEN SURROUNDING PARTICLE

It is useful to correlate the percent $O_2$ in the environment of a burning char particle with the overall percent stoichiometric air used for the coal which formed the char. This can be done using a mass balance and the composition of Utah King Mine Coal ($C=72.3\%$ wt, $H=5.8\%$ wt, $N=1.3\%$ wt, $S=0.5\%$ wt, $O=14.9\%$ wt, Ash=$5.2\%$ wt,) and the resulting char composition given by McCann et al. (1971) ($C=81.6\%$ wt, $H=1.0\%$ wt, $N=1.4\%$ wt, $S=0.5\%$ wt, $O=2.3\%$ wt, Ash=$13.2\%$ wt). In the calculations the pounds of char formed from one pound of coal were calculated by assuming all the ash went to the char and that all volatile carbon is converted to $CO_2$. A simple mass balance then provided the point shown in Figure B-1, in which the percent $O_2$ in the char environment is plotted against the overall percent stoichiometric air for the coal.
Figure B-1. Relationship Between Composition of Gas Surrounding Char Particle and Stoichiometric Air Percent
APPENDIX C

INFORMATION COLLECTED FROM CHARFCO AND CHARFNO

Tables C1 and C2 are presented in order to give an example of the type of information collected from CHARFCO and CHARFNO. The specific runs shown here are those describing the coupled effect of changing particle size and free stream oxygen content and is used as a basis for Table 5 in the text.
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NOMENCLATURE

AL2 : Position of numerical instability in the calculation of CO production \( \text{cm} \)

AL3 : Position of numerical instability in the calculation of NO production \( \text{cm} \)

\( A_0 \) : Surface reaction rate constant \( \frac{\text{cm}}{\text{sec}} \)

\( A_1, A_2, A_3 \) : Coefficients to calculate Diffusivities of O\(_2\), CO and NO respectively \( \frac{\text{cm}^2}{\text{sec}^{0.15}} \)

\( B_1, B_2 \) : Constants of integration

\( C_1, C_2, C_3 \) : Concentration of O\(_2\), CO and NO respectively \( \frac{\text{gm mole}}{\text{cc}} \)

\( C^0_1, C^0_2, C^0_3 \) : Initial concentration of O\(_2\), CO and NO respectively \( \frac{\text{gm mole}}{\text{cc}} \)

\( C_{1f}, C_{2f}, C_{3f} \) : Final concentration of O\(_2\), CO and NO respectively \( \frac{\text{gm mole}}{\text{cc}} \)

\( C^*_1, C^*_2, C^*_3 \) : Calculated final mole fraction of O\(_2\), CO and NO respectively

\( D_{ij} \) : Diffusivities of species i in N\(_2\) \( \frac{\text{cm}^2}{\text{sec}} \)

\( E_1 \) : Activation energy Reaction I \( \frac{\text{cal}}{\text{gm mole}} \)

\( E_2 \) : Activation energy Reaction IV \( \frac{\text{cal}^2}{\text{gm mole}} \)

\( h_{ip} \) : Thiele Parameter for pore, dimensionless

\( h_{if} \) : Thiele parameter for film, dimensionless

\( k \) : Boltzmann constant \( \frac{\text{gm - cm}^2}{\text{sec}^{6}K} \)
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<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
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<tr>
<td>$K_{eff}$</td>
<td>Effective rate coefficient</td>
<td>( \frac{1}{\text{sec}} )</td>
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<td>$K_S$</td>
<td>Surface reaction rate coefficient</td>
<td>( \frac{\text{gm}}{\text{cm}^2 \cdot \text{sec} \cdot \text{atm}} )</td>
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<td>Kinetic rate coefficient Reaction II</td>
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<td>Pore length</td>
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<td>$M_i$</td>
<td>Molecular weights</td>
<td>( \text{gm mole} )</td>
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<td>$N\text{O}_x$</td>
<td>Flux of $O_2$</td>
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<td>$P$</td>
<td>Pressure</td>
<td>( \text{atm} )</td>
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<td>$q$</td>
<td>Correction factor dimensionless</td>
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<td>$r$</td>
<td>Radius of pore</td>
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<td>$R$</td>
<td>Universal gas constant</td>
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<td>( \frac{\text{gm} - \text{mole}}{\text{sec}} )</td>
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<td>$R_{\text{CO}}$</td>
<td>Rate of consumption of CO</td>
<td>( \frac{\text{cc}^{1.5}}{\text{gm mole}^{1.5} \cdot \text{sec}} )</td>
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<td>$RF$</td>
<td>Film radius</td>
<td>( \text{cm} )</td>
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<td>$RI$</td>
<td>Particle radius</td>
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<td>$R_{\text{NO}}$</td>
<td>Rate of consumption of NO</td>
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<td>Residual function for $\text{CHARP}CO$ and $\text{CHARFC}CO$ dimensionless</td>
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RES**: Residual function for CHARPNO and CHARFNO dimensionless

t: Time  

T: Temperature  °K

x: Distance inside the pore  cm

α_i: Difference in concentration  gm mole/cc

δ: Thickness of film  cm

ε_ij: Maximum attractive energy between two molecules  gm cm²/sec²

ζ: Function of thickness and dimensionless radius  cm

η : Dimensionless length  gm mole/cm - sec

θ: Summation of fluxes  gm mole/sec

ρ: Molar density  gm mole/sec

σ_ij: Collision diameter  cm

φ: Dimensionless radius

ψ_i: Dimensionless concentration

Ω_{DiJ}: Dimensionless function of temperature and intermolecular potential
LITERATURE CITED


