Numerical Modelling of One-Dimensional Laminar Pulverized Coal Combustion

Phần II
(1995)

Trịnh Minh Chính
1. INTRODUCTION

Research into coal dust combustion has been going on for almost a century. Everybody agrees that coal particles burn in a very complicated manner. The combustion process includes devolatilization (pyrolysis), homogeneous reactions (reactions of volatile components), heterogeneous reactions (surface reactions or char oxidation), swelling, cracking, etc. Many research workers have attempted to simplify the process by deviding it into several subprocesses, e.g. devolatilization, char oxidation, etc..

Kobayashi et al. (1976) measured weight loss of lignite and bituminous coal by devolatilization at high temperatures. They proposed a pyrolysis model which consists of two competing overall reactions instead of a single first-order reaction. According to Pitt (1962), any theory of the kinetics of coal pyrolysis must be based on a number of simplifying assumptions, namely that coal is a mixture of many components which decompose independently, and that the composition reactions have a wide range of activation energies. He developed a new model for coal devolatilization called Distributed Energy Activation Model (DAEM), based on total volatiles. Anthony et al. (1974) correlated their experimental data of lignite and bituminous coals to find parameters for this model. Solomon et al. (1988) suggested a model applicable for all volatile components, e.g. CO, H₂O, CO, HCN, C₂H₆, H₂, etc. There are many models of coal devolatilization such as multiple parallel reaction model (MPRM), distributed activation energy model (DAEM), multiple competing reaction model (MCRM), consecutive competing char-forming reactions model, etc. Reviews of devolatilization of coal particles are described in Saxena (1990), Solomon et al. (1992), Essenhigh (1981) and Anthony and Howard (1976).

The combustion of volatile components is very complicated. The DAEM and MPRM may give more details of volatile components compared with the other models. However, the composition of volatiles (mass fractions of single volatile or volatile components) for different types of coal are usually unknown and they must be calculated. Some simple methods have been mentioned in Gray et al. (1976). The composition of volatiles in this report was calculated by an interpolated method (APP.A1). It is based on the experimental data of Solomon et al. (1992).

Reactivity and combustion of coal chars is also a complicated subject. The burning rate of coal char depends on the rate of transport of oxygen to the external surface of the particle to react with fixed carbon and form both CO and CO₂. CO begins to burn if the temperature is greater than about 923 K, and CO is the sole heterogeneous product when the particle temperature is above 1373 K. According to Saxena (1990), two important questions in establishing the combustion mechanism for a given combustion system are first, what are the combustion products on the char particle's surface? and second, which of the two gases, oxygen or carbon dioxide, should preferably diffuse to the surface? From this information, several models, e.g. one-film, two-film and continuous-film are proposed, depending on the behaviour of CO and CO₂ at the boundary layers surrounding small particles. According to Mitchell et al. (1990), no definitive experimental data exist at high temperatures to establish
the relative importance of CO2 formation on the surfaces of particles and CO2 formation in the boundary layers surrounding particles in the pulverized-coal size range.

The term "modelling", according to Spalding (1963), is used to connote the practice of predicting the likely results of one experiment by way of the interpretation of the results of another experiment. Modelling of coal combustion, including pyrolysis, combustion of volatiles, char oxidation, soot formation and burning, mass transfer, heat transfer, etc., is a very complicated matter. Several models for pyrolysis, char oxidation, and a number of reactions for volatile oxidation have been proposed. Each model has several empirical constants which are found under certain conditions. These constants or models must be tested in different cases with different conditions.

Smoot et al. (1976a) have studied the propagation of laminar, coal-dust air flames. They predicted flame velocity, temperature, species concentration (CO, CO2, H2O, H2, H, OH, O, O2) and particle diameter. Effects of gaseous diffusion, coal pyrolysis, char oxidation, and gaseous reactions were considered. Smith and Smoot (1980) have developed a one-dimensional model for pulverized coal combustion and gasification processes. The heat transfer between gas and particles, particles and particles, devolatilization and char oxidation were described very thoroughly. Smoot (1984,1991) made a review of models for pulverized coal combustors/gasifiers, one-dimensional and multidimensional coal reactors, fixed bed and one-dimensional fluidized bed.

In this report, both Illinois #6 and Pittsburgh #8 coals were tested. Two devolatilization models called multiple parallel reaction model (MPRM) and distributed activation energy model (DAEM) have been used for the investigation. The char oxidation model is described by a single-film model, i.e. both CO and CO2 are the heterogeneous products and CO reacts with oxygen after it has been transported to the free stream. Two different "reaction rates" were tested. The first one called char oxidation model 1 or Mitchell's model is described in Mitchell (1988) and the second, simple model called char oxidation model 2, is described in Field et al. (1967). It is called a simple model because the apparent reaction order equals unity. Six sets of kinetic reaction model are described for combustion (oxidation) of active volatile components (CO, C2H6, CH4, H2 and HCN). They are called global model, reduced model 1, 2, 3 and 4, and elementary model. They varied from 3 reactions (global model) to 123 reactions (elementary model). Except for the elementary model, all kinetic reaction models were tested with and without the simple char oxidation model. The elementary model with 123 reactions is too comprehensive to be calculated with the char oxidation model. Different oxygen concentrations in oxidizer and different particle sizes are investigated. The influences of radiation of particles to a cold environment and radiation between particles are also considered.

The governing equations, devolatilization models, and char oxidation models are described in detail. APP.A1 shows the method for calculating the composition of volatiles. The numerical calculation of DAEM for the non-isothermal process is described in APP.A2. The solver method (Newton-Rapshon method) for oxidation model 1 (Mitchel's model) is
described in the subsection "Combustion of Coal Char".

Results from the calculations were compared with experimental data. These comparisons are shown in concentration and temperature profile figures. Some of the particle profiles obtained with different methods are also compared with each other as well as with experimental data, and are shown in the section "Results and discussions". APP.B1 shows the results of the calculations for Illinois #6 coal air flame. APP.B2 shows the results of the calculations for Pittsburgh #8 coal air flame.

APP.C shows the figures of the proximate and ultimate analysis (dry-ash-free basic) of coal char, weight loss of chemical elements of coal char as a function of particle mass loss, and particle mass and mass loss of coal particles in coal air flames. These figures are purely illustrative and therefore need no comment.

APP.D shows the analysis of particle sizes for six coal types: Blair Athol, Cerrejon, Illinois #6, Middleburgh, Pittsburgh #8 and Ulan.
2 MATHEMATICAL MODEL

In order to overcome the complexity of pulverized-coal combustion, including fluid mechanics, devolatilization, heterogeneous (particles and gas) and homogeneous (gas) reactions, a model is developed with the following assumptions:
1- The flow is one-dimensional, steady, and premixed.
2- The measured gas temperatures are used to compute reaction rates. The gas temperatures are known (measured) so that they cannot influence the kinetic (homogeneous) reactions.
3- The velocities of gas and particles are equal.
4- Body forces and viscous forces within the gas phase are disregarded.
5- Coal particles are treated as spheres.
6- Tar and soot formations are not considered.
7- Swelling formation is not considered.
8- The particle size is constant and equals the mass-mean particle size.
9- The particle temperature is uniform.
10- Oxygen is transported to the surface and products are transported away by molecular diffusion.
11- Molecular diffusion in the gas phase is not influenced by the presence of coal particles.

2.1 Governing equations
The governing equations for one-dimensional laminar coal combustion (Fig. 2.1) can be expressed as follows.

2.1.1 Particle phase
Mass balance equation
\[
\frac{dM_{pj}}{dx} + \frac{A_{tot}}{V_{tot}} \{ n_j A_{pj} q + M_{pj,0} \sum_{i=1}^{L} Y_i \} = 0
\]  

Energy balance equation
\[
M_{pj} C_{pj} \frac{dT_p}{dx} - \frac{A_{tot}}{V_{tot}} n_j A_{pj} \frac{B}{1 - e^{-\frac{B}{T_p}}} h_g (T_g - T_p) + A_{tot} \left( \frac{dq^+}{dx} - \frac{dq^-}{dx} \right) - \frac{A_{tot}}{V_{tot}} n_j A_{pj} q H_{eff} + \frac{A_{tot}}{V_{tot}} Q_w = 0
\]  

where x is the spatial coordinate; \( M_{pj} \) is the mass flow rate of particles; \( A_{tot} \) is the cross-sectional area; \( V_{tot} = A_{tot} dx \) is the volume; \( n_j \) is the number of particles per cm\(^3\); \( q \) is the overall particle burning rate (the rate of consumption of carbon); \( M_{pj,0} \) is the initial particle mass; \( Y_i \) is the mass fraction of species \( i \), released by pyrolysis; \( T_p \) is the particle temperature; \( C_{pj} \) is the constant pressure heat capacity of particles; \( A_{pj} \) is the particle surface area; \( h_g \) is the heat transfer coefficient; \( T_g \) is the gas temperature; \( q_r \) is the radiative heat flux between particles; \( H_{eff} \) is the effective heat of reaction; \( Q_w \) is the radiative heat transfer from hot particles to the cold environment.
The first term on the left side of Eq.(1) is the mass rate of change of particles. The second term is particle mass loss due to char burning. The last term is particle mass loss due to pyrolysis. The first term on the left side of Eq.(2) is the change of particle temperature. The second term, the convection term, is the heat transfer between particles and gas. The third term is the radiative heat transfer between particles. The next term is the production (source) term, the energy being generated by the burning of char. The last term is the energy, which is lost in a cold environment.

The effective heat of reaction $H_{\text{eff}}$ can be calculated from the heat of combustion of the two reactions, $C + \frac{1}{2}O_2 = CO$ and $C + O_2 = CO_2$.

$$H_{\text{eff}} = \psi \cdot H_{CO} + (1 - \psi) \cdot H_{CO}$$  

where $\psi$ and $(1-\psi)$ are the fractions of the carbon content of the particle to be converted to $CO_2$ and $CO$ at the particle surface. $H_{CO}$ and $H_{CO2}$ are the heat of reaction per mole carbon for the reactions $C + \frac{1}{2}O_2 = CO$ and $C + O_2 = CO_2$, respectively. $H_{CO} = 9.79 \times 10^{10}$ ergs/g (2340.0 cal/g) and $H_{CO2} = 33.05 \times 10^{10}$ ergs/g (7900.0 cal/g) (Ayling and Smith (1972)).

The heat transfer coefficient is defined as

![Figure 2.1: Flat-flame burner schematic](image)
where $Nu$ is the Nusselt number; $\lambda_g$ is the thermal conductivity of the mixture, and $d_p$ is the particle diameter. For a spherical particle in the gas stream, $Nu$ is found as (Ranz and Marshall (1952))

$$Nu = 2.0 + 0.6 \frac{Re^\frac{1}{2}}{Pr^{\frac{1}{2}}}$$

(5)

$Nu$ is given as 2 since particle and gas have the same velocities.

The radiative influence on particles by the cold environment is

$$Q_w = n_j A_{pj} \varepsilon \sigma (T_p^4 - T_w^4)$$

(6)

$\varepsilon$ is the particle emissivity; $\sigma$ is the Stefan-Boltzmann constant; $T_w$ is the temperature of the room wall.

By considering the influence of mass transfer on heat transfer using film theory, the Stefan flow parameter $B$ is found as (Water et al. (1988a,a988b))

$$B = \frac{(1 - v) q d_p C_{pj}}{2 M \varepsilon \lambda}$$

(7)

where $v$ is the oxygen stoichiometric coefficient. For small particles, $B$ can be taken as 1.

The specific heat at constant pressure (constant pressure heat capacity) of the particles in the flame is calculated by JANAF Thermochemical Tables

For $T_p = 300 - 1000K$:

$$C_{pj}/R = -0.6705661 + 0.07181499E-1T - 0.05632921E-4T^2$$

$$+ 0.02142298E-7T^3 - 0.04168562E-11T^4$$

For $T_p = 1000 - 5000K$:

$$C_{pj}/R = 1.49016640 + 0.16621256E-2T - 0.06687204E-5T^2$$

$$+ 0.12908796E-9T^3 - 0.09205334E-13T^4$$
Figure 2.2: Specific heat of particles in Illinois #6 coal air flame.

Figure 2.2 shows the calculated specific heat of the carbon in Illinois #6 coal air flame. The specific heat of particles varies from 0.7 for $T_p = 298\text{K}$ to 2.1 kJ/(kg K) for $T_p = 1771\text{K}$. It is clear that the specific heat of particles cannot be taken as a constant.

The particle temperatures calculated with constant and varied $C_{pj}$ are shown in Fig.3.3 (see section 3 Results and Discussions). The difference particle temperature calculated with two different $C_{pj}$ is about 50.0 K (near the peak of the temperature profile).

2.1.2 Radiative model

The two-flux model of radiative heat transfer between particles can be written as (Siddal (1974))
q$^+$ and q$^-$ are the radiative heat fluxes in positive and negative directions, respectively (Fig.2.3). On the left-hand side of Eq.(8) is the change of q$^+$. The first term on the right-hand side is the extinction of q$^+$ due to absorption and back-scattering. The next term is the source term due to hot particles which emit radiation. The last term is the back scattering of q$^-$ contributing to the q$^+$. The interpretation of Eq.(9) is similar to that for Eq.(8), but in the opposite direction.

Combining Eqs.(8) and (9) yields

$$\frac{dq^+}{dx} - \frac{dq^-}{dx} = -2\left(\sigma_a + b\sigma_s\right)q^+ + 2\sigma_a \sigma T_p^4 + 2b\sigma_s q^-$$

(10)

where

$$\sigma_a = C_a \frac{\pi}{4} d_p^2 n_j$$

(11)

$$\sigma_s = C_s \frac{\pi}{4} d_p^2 n_j$$

(12)

$\sigma_a$ and $\sigma_s$ are the absorption and scattering coefficients for monodisperse coal dust cloud, respectively; $C_a$ is the absorption constant; $C_s$ is the scattering constant.

### 2.1.3 Gas phase

The mass balance equation

$$\frac{dM_g}{dx} V_{tot} \left\{ \sum_{i=1}^{K} Y_i \delta A_{pj,i} q + \dot{M}_{pj,i} \sum_{i=1}^{K} Y_i \right\} = 0$$

(13)

The energy balance equation (this equation is not used in the calculations)

$$\dot{M}_g \frac{dT_g}{dx} \frac{l}{C_p} \left\{ \lambda A_{tot} \frac{dT_g}{dx} \right\} + \frac{\dot{M}_{tot}}{C_p} \rho \sum_{i=1}^{K} Y_i V_k C_{pk} \frac{dT_g}{dx}$$

$$+ A_{tot} \sum_{i=1}^{K} \dot{\omega}_k h_k W_k + \frac{A_{tot}}{C_{pg}} \left\{ \frac{1}{C_p} \sum_{i=1}^{K} n_j A_{pj,i} B \right\} - \frac{\dot{\omega}_k}{C_p} (T_g - T_p) = 0$$

(14)

Species conservation

$$\dot{M}_g \frac{dY_k}{dx} + \frac{d}{dx} \left\{ \rho A_{tot} Y_k V_k \right\} - A_{tot} \dot{\omega}_k W_k = 0$$

(15)

where

$$\rho = \frac{\rho W}{RT}$$

(16)

$M_g$ is the mass flow rate of gas; $C_p$ is the constant pressure heat capacity of the mixture; $Y_k$ is the mass fraction of the kth species (there are K species); $C_{pk}$ is the constant pressure
heat capacity of the kth species per unit volume; $\dot{\omega}$ is the molar rate of production by chemical reaction of the kth species per unit volume; $h_k$ is the specific enthalpy of the kth species; $W_k$ is the molecular weight of the kth species; $\bar{W}$ is the mean molecular weight of the mixture; $R$ is the universal gas constant; $V_k$ is the diffusion velocity of the kth species.

Fig. 2.4 shows the calculated gas mass density in Illinois #6 coal air flame. The gas mass density decreases from 0.001185 g/cm³ at $x = -1$ cm (distance before the burner outlet, $T_g = 298$ K) to 0.000898 g/cm³ at $x = 0$ cm (at the burner outlet, $T_g = 410$ K) and 0.000180 g/cm³ at $x = 0.5$ cm ($T_g = 1770$ K), and it increases to 0.000232 g/cm³ at $x = 3$ cm ($T_g = 1327$ K). Table 2.1 shows the gas mass density in coal air flame and the air density for the same gas temperature. The difference between them is about 10% at the high temperature ($T = 1770.0$ and 1340.0 K). At the low temperature ($T = 298.0$ and 410.0 K), the gas density and air density have the same values due to the air being present only in the gas phase of the flame.

<table>
<thead>
<tr>
<th>$T_g$ (K)</th>
<th>298.0</th>
<th>410.0</th>
<th>1770.0</th>
<th>1340.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X$ (cm)</td>
<td>-1.0</td>
<td>0.0</td>
<td>0.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Gas mass density (g/cm³)</td>
<td>0.001185</td>
<td>0.000852</td>
<td>0.000180</td>
<td>0.000232</td>
</tr>
<tr>
<td>Air density (g/cm³)</td>
<td>0.001185</td>
<td>0.000852</td>
<td>0.000197</td>
<td>0.000260</td>
</tr>
</tbody>
</table>

Table 2.1: Comparison between gas density in coal air flame and air density.

Figure 2.4: The calculated gas mass density in Illinois #6 coal air flame.

The diffusion velocity, $V_k$, may be composed of three parts: the ordinary diffusion velocity, $V_{kd}$, the non-zero thermal diffusion velocity, $V_{kt}$, and the correction velocity, $V_c$. 
\[ V_k = V_{kd} + V_{kt} + V_c \] (17)

\[ V_{kd} \] is given by Curtiss and Hirschfelder (1949) as

\[ V_{kd} = -D_k \frac{dX_k}{dx} \] (18)

where \( X_k \) is the mole fraction, and where the mixture-averaged diffusion coefficient \( D_k \) is given explicitly in terms of the binary diffusion coefficient \( D_{jk} \).

\[ D_k = \frac{1 - Y_k}{\sum_{j \neq k} \frac{X_j}{D_{kj}}} \] (19)

The non-zero thermal diffusion velocity \( V_{kt} \) is given

\[ V_{kt} = \frac{D_{kT}}{X_k} \frac{1}{T} \frac{dT}{dx} \] (20)

where \( k_{T} \) is the thermal diffusion ratio (Chapman and Cowling (1970)).

The correction velocity \( V_c \) (independent of species but a function of \( x \)) is included to ensure that the mass fractions total unity. More details of diffusion velocities can be seen in Kee et al. (1985,1992).

2.1.4 Chemical reaction rate expressions (Kee et al. (1985))

Consider \( i \) elementary reversible (or irreversible) reactions involving \( K \) chemical species that can be represented in the general form

\[ \sum_{k=1}^{K} V_{k,i} X_k = \sum_{k=1}^{K} V_{k,i} X_k \quad (i = 1, \ldots, I) \] (21)

the stoichiometric coefficient \( v_{ki} \) are integers and \( \chi_k \) is the chemical symbol for the \( k \)th species.

The production rate \( \omega_k \) of the \( k \)th species can be written as a summation of the rate-of-progress variables for all reactions involving the \( k \)th species:

\[ \dot{\omega}_k = \sum_{i=1}^{I} v_{ki} q_i \quad (k = 1, \ldots, K) \] (22)
The rate-of-progress variable \( q_i \) for the \( i \)th reaction is given by the difference of the forward rates and the reverse rate as
\[
q_i = k_{f_i} \prod_{k=1}^{K} X_k^{\nu_{ki}} - k_{r_i} \prod_{k=1}^{K} X_k^{\nu_{ki}}
\]
(24)

where \([X_k]\) is the molar concentration of the \( k \)th species and \( k_{f_i} \) and \( k_{r_i} \) are the forward and reverse rate constants of the \( i \)th reaction. The forward rate constants for the \( I \) reactions are generally assumed to have the following Arrhenius temperature dependence:
\[
k_{f_i} = A_i T^\beta_i \exp\left(\frac{-E_i}{RT}\right)
\]
(25)

where \( A_i \) is the pre-exponential factor, \( \beta_i \) is the temperature exponent, and \( E_i \) is the activation energy.

The reverse rate constants \( k_{r_i} \) are related to the forward rate constants through the equilibrium constant as
\[
k_{r_i} = \frac{k_{f_i}}{K_{ci}}
\]
(26)

Although \( K_{ci} \) is given in concentration units, the equilibrium constants are more easily determined from the thermodynamic properties in pressure units; they are related by
\[
K_{ci} = K_{pi} \left( \frac{P_{atm}}{RT} \right)^{\sum_{j=1}^{K} \nu_{ji}}
\]
(27)

where \( P_{atm} \) denotes a pressure of 1 atm. The equilibrium constants \( K_{pi} \) are obtained with the relationship
\[
K_{pi} = \exp\left(\frac{\Delta S_i^o}{R} - \frac{\Delta H_i^o}{RT}\right)
\]
(28)

the \( \Delta \) refers to the change that occurs in passing completely from reactants to products in the \( i \)th reaction. More specifically,
2.1.5 Discretization (Kee et al. (1985))

All partial differential equations are rewritten to a system of algebraic equations by using the finite difference approximation. The initial approximations are usually on a very coarse mesh that may have few points. After obtaining a solution on the coarse mesh, new mesh points are added in regions where the solution or its gradients change rapidly.

An initial guess for the solution on the finer mesh is obtained by interpolating the coarse mesh solution. This procedure continues until no mesh points are needed to resolve the solution to the degree specified by the user. The system of algebraic equations is solved by the damped modified Newton algorithm. However, if the Newton algorithm fails to converge, the solution estimate is conditioned by a time integration. This provides a new starting point for the Newton algorithm that is closer to the solution, and thus more likely to be in the domain of convergence for Newton’s method.

The upwind (windward) difference scheme is used on the convective terms, while the second-order centered differentiation is used on the diffusive term. The diffusive term in the species conservation equation is approximated in a similar way, but it appears to be different because of the diffusion velocities. More details concerning discretization can be found in Kee et al. (1985).

2.1.6 Boundary conditions

At the cold boundary (inlet), the mass flux fractions and the temperature can be written

\[
Y_{k,j}^* + (p A Y_k V_k)_{j-l} = 0
\]

and

\[
T_{j} = T_b = 0
\]

where \( T_b \) is the specified burner temperature. At the hot boundary (outlet), all gradients vanish, i.e.

\[
\frac{Y_{k,j}}{x_j} = 0
\]

and

\[
\frac{T_{k,j}}{x_j} = 0
\]

At the cold and hot boundaries, the radiative heat fluxes in positive and negative directions are
\[
\begin{align*}
  x < 0: & \quad q^+ = 0 ; \quad q^- = 0 \\
  x \geq 0: & \quad q^+_0 = e \sigma T_p^i ; \quad q^-_0 = q^-_i \\
  x \geq 0: & \quad q^+_j = q^+_j T_p^i ; \quad q^-_j = \sigma T_p^i
\end{align*}
\]  

(35)  

(36)  

(37)

where \( q_0^+ \) and \( q_0^- \) are the flux densities at the burner outlet; \( q_i^- \) is the flux density at the first node point after the burner outlet; \( q_i \) is the flux at the end of the flame; \( T_p \) is the particle temperature.

### 2.2 Coal devolatilization (pyrolysis)

Coal devolatilization is important in a coal conversion process. The volatiles, which can account for up to 70% of the coal's weight loss, control the ignition, the temperature and the stability of the flame in combustion (Water et al. (1988a)). According to Field et al. (1967), when coal is heated to a sufficiently high temperature it begin to decompose, producing tars and gases and volatiles. The volatiles consist of a mixture of combustible gases, carbon dioxide, and water vapour. Apart from carbon monoxide and hydrogen the combustible gases are mainly hydrocarbons, although there are small quantities of phenolic and other compounds. The volatile yield and composition are influenced by the coal rank and type, and for example, by the externally specified variables such as particle size, heating rate, time-temperature history and pressure (Carpenter and Skorupska (1993)). The decomposition process with the heating rates less than or equal 10 °C/min is called slow decomposition (used in industrial carbonization processes) and the decomposition with the heating rates higher than those of slow decomposition is called rapid decomposition (as happens in most combustion systems, e.g. fluidized bed, fixed bed, pulverized coal furnaces, etc.) (Field et al. (1967)).


According to Anthony and Howard (1976), several authors at different times have reviewed many of the diverse findings, each time identifying new aspects of the problem and new directions for research. The recent acceleration of coal research has generated much new information which must be reconciled and reviewed. A number of models of coal pyrolysis have been proposed, e.g., a) Single Reaction: nth-Order Arrhenius reaction, Non-
Arrhenius model; b) Multiple Parallel Reaction: Two first-order Arrhenius reactions, Multiple first-order reactions with statistical distribution of activation energies; c) Multiple Competing Reactions: Two-first-order reactions, Multiple first-order reaction; d) Complex Schemes: Multiple consecutive parallel first-order reactions, Parallel competing first-order reactions; e) Schemes involving secondary char-forming reactions: Consecutive competing char-forming reactions, Parallel competing char-forming reactions. More details of these models can be found in Essenhigh (1981).

Here is a brief description of the multiple parallel reaction model (MPRM) and distributed activation energy model (DAEM), which are used in the calculations.

### 2.2.1 Multiple Parallel Reaction Model (MPRM) (Anthony et al. (1974))

a) Model based on total volatiles

The simplest model for coal devolatilization based on the quantity of volatiles (total weight loss by the particles) can be expressed as

\[
\frac{dV}{dt} = k (V^* - V)
\]  

where \( V \) is the mass of volatiles, per mass of original coal, evolved at time \( t \), \( V^* \) is the value of \( V \) at \( t = \infty \) and \( k \) is the rate constant. It may be written

\[
k = k_0 \exp\left\{ -\frac{E}{RT} \right\}
\]

where \( k_0 \) is the apparent frequency factor, \( E \) is the activation energy, \( R \) is the ideal gas constant, and \( T \) is the absolute temperature. \( k_0 = 6.5 \times 10^{16} \ \text{sec}^{-1} \), \( E = 36.89 \ \text{kcal/mole} \) (Anthony et al. (1974)). For a given set of conditions, values of \( k \) from various authors may differ by several factors of 10 and \( E \) may vary from several kcal/mole to nearly 50 kcal/mole.

b) Model based on individual volatile constituents

Pitt (1962) assumed that coal decomposes thermally as if it were a mixture of many pseudospecies, each of which decomposes via an independent first-order reaction and with a characteristic energy, i.e. (Saxena (1990))

\[
\frac{dV_i}{dt} = k_i (V_{i}^* - V_i)
\]  

where

\[
k_i = k_0 \exp\left\{ -\frac{E_i}{RT} \right\}
\]  

subscript \( i \) denotes the composition of the volatile matter, e.g. \( \text{CO}_2, \text{CO}, \text{H}_2\text{O}, \) etc. The rate
constants for MPRM are shown in Table 2.2.

<table>
<thead>
<tr>
<th>Species</th>
<th>$k_0$ [sec$^{-1}$]</th>
<th>$E_0$ [kcal/mol]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>$6.5 \times 10^{16}$</td>
<td>67.0</td>
<td>[69,84]</td>
</tr>
<tr>
<td>CO</td>
<td>$2.2 \times 10^{18}$</td>
<td>60.0</td>
<td>[69,84]</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>$1.4 \times 10^{18}$</td>
<td>79.0</td>
<td>[69,84]</td>
</tr>
<tr>
<td>HCN</td>
<td>$1.7 \times 10^{13}$</td>
<td>59.6</td>
<td>[69,84]</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>$8.4 \times 10^{14}$</td>
<td>59.1</td>
<td>[69,84]</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>$7.5 \times 10^{13}$</td>
<td>59.0</td>
<td>[69,84]</td>
</tr>
<tr>
<td>H$_2$</td>
<td>$1.0 \times 10^{14}$</td>
<td>80.0</td>
<td>[69,83,84]</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>$1.2 \times 10^{12}$</td>
<td>13.7</td>
<td>[69,83,84]</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>$2.91 \times 10^{9}$</td>
<td>36.89</td>
<td>[1]</td>
</tr>
<tr>
<td>Tar</td>
<td>$4.3 \times 10^{14}$</td>
<td>54.6</td>
<td>[69]</td>
</tr>
<tr>
<td></td>
<td>$8.6 \times 10^{14}$</td>
<td>27.5</td>
<td>[84]</td>
</tr>
</tbody>
</table>

Table 2.2: The rate constants of MPRM based on individual volatile constituents. These constants are taken from DAEM with the standard deviations, $\sigma_v$, are set zeroes.

2.2.2 Distributed Activation Energy Model (DAEM) (Anthony et al. (1974), Saxena (1990), Serio et al. (1987), Solomon et al. (1988,1992))

a) Model based on total volatiles

DAEM can also be called multiple first-order reactions with statistical distribution of activation energies. The activation energy, $E$, in Eq.(39) is expressed as a continuous distribution function $f(E)$ so that $f(E)\,dE$ is the fraction of potential volatiles having an activation energy between $E$ and $E + dE$. Hence for all volatiles

$$dV^* = V^* \, f(E) \, dE$$ \hspace{1cm} (42)

with

$$\int_{\sigma}^{\infty} f(E) \, dE = 1$$ \hspace{1cm} (43)

Anthony et al. (1974) proposed a Gaussian distribution for the activation density function $f(E)$ so that
Combining Eqs. (42), (43) and (44) yields

\[
f(E) = \frac{1}{\sigma (2\pi)^{\frac{1}{2}}} \exp \left\{ -\frac{(E - E_0)^2}{2\sigma^2} \right\} \tag{44}
\]

For simplicity, the integral limits were changed to \(E_0 \pm 2\sigma\) which includes 95.5% of the reaction set. Eq. (45) then becomes

\[
\frac{V^* - V}{V^*} = \int_{E_{\text{min}}}^{E_{\text{max}}} \exp \left\{ \int_0^t k \, dt \right\} f(E) \, dE \tag{45}
\]

\(E_0\) is the mean activation energy. \(\sigma\) is the standard deviation. \(E_{\text{min}} = E_0 - 2\sigma\) and \(E_{\text{max}} = E_0 + 2\sigma\).

where \(k_0 = 6.5 \times 10^{16} \text{ sec}^{-1}\), \(E = 36.89 \text{ kcal/mole}\) and \(\sigma = 4.18 \text{ kcal/mole}\) (Anthony et al. (1974)).

For the isothermal process, Eqs. (45) and (46) become

\[
\frac{V^* - V}{V^*} = \int_{E_{\text{min}}}^{E_{\text{max}}} \exp \left\{ \int_0^t k \, dt \right\} f(E) \, dE \tag{47}
\]

\[
\frac{V^* - V}{V^*} = \int_{E_{\text{min}}}^{E_{\text{max}}} \exp \left\{ \int_0^t k \, dt \right\} f(E) \, dE \tag{48}
\]

\(h)\) Model based on individual volatile constituents

The DAEM for the nonisothermal process based on individual volatile constituents can be written

\[
\frac{V_{i^*} - V_i}{V_i} = \int_{E_{\text{min}}}^{E_{\text{max}}} \exp \left\{ \int_0^t k_i \, dt \right\} f(E_i) \, dE_i \tag{49}
\]

or

\[
\frac{V_{i^*} - V_i}{V_i} = \int_{E_{\text{min}}}^{E_{\text{max}}} \exp \left\{ \int_0^t k_i \, dt \right\} f(E_i) \, dE_i \tag{50}
\]

where

\[
k_i = k_0 \exp \left\{ \frac{E_i}{RT} \right\} \tag{51}
\]
\[ f(E_i) = \frac{1}{\sigma_i (2\pi)^{\frac{3}{2}}} \exp \left\{ -\frac{(E_i - E_0)^2}{2\sigma_i^2} \right\} \]  

(52)

For the isothermal process, Eqs.(49) and (50) become

\[ \frac{V^* - V_i}{V^*} = \int_0^{\infty} \exp\{-k_i t\} f(E_i) dE \]

(53)

\[ \frac{V^*_i - V_i}{V^*_i} = \int_{E_{i_{\text{min}}}}^{E_{i_{\text{max}}}} \exp\{-k_i t\} f(E_i) dE \]

(54)

The rate constants for this model are shown in Table 2.3

### 2.2.3 Q-factor

The yield of volatiles in the models was greater than the potential yield indicated by the proximate volatile matter of the coal. Jensen and Mitchell (1993) defined the Q-factor as the ratio of actual volatile yield to the proximate volatile matter. They measured the volatiles release in 6 and 12 mole-% oxygen environments for 9 different coal types (Table 2.4 (dry basic) and Table 2.5 (dry-ash-free basic)). More details are given in (Essenhigh (1981)).

\[ Q\text{-factor} = \frac{\text{Actual volatile yield}}{\text{Proximate volatile matter}} \]

(55)

<table>
<thead>
<tr>
<th>Species</th>
<th>( k_0 ) ([\text{sec}^{-1}])</th>
<th>( E_0 ) ([\text{kcal/mol}])</th>
<th>( \sigma ) ([\text{kcal/mol}])</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>( 6.5 \times 10^{16} )</td>
<td>67.0</td>
<td>3.0</td>
<td>[69,84]</td>
</tr>
<tr>
<td>CO</td>
<td>( 2.2 \times 10^{18} )</td>
<td>60.0</td>
<td>3.0</td>
<td>[69,84]</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>( 1.4 \times 10^{18} )</td>
<td>79.0</td>
<td>11.8</td>
<td>[69,84]</td>
</tr>
<tr>
<td>HCN</td>
<td>( 1.7 \times 10^{13} )</td>
<td>59.6</td>
<td>3.0</td>
<td>[69,84]</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>( 8.4 \times 10^{14} )</td>
<td>59.1</td>
<td>3.0</td>
<td>[69,84]</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>( 7.5 \times 10^{13} )</td>
<td>59.0</td>
<td>3.9</td>
<td>[69,84]</td>
</tr>
<tr>
<td>H(_2)</td>
<td>( 1.0 \times 10^{14} )</td>
<td>80.0</td>
<td>12.5</td>
<td>[69,83,84]</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>( 1.2 \times 10^{12} )</td>
<td>13.7</td>
<td>1.5</td>
<td>[69,83,84]</td>
</tr>
<tr>
<td>H(_2)S</td>
<td>( 2.91 \times 10^9 )</td>
<td>36.89</td>
<td>4.18</td>
<td>[1]</td>
</tr>
<tr>
<td>Tar</td>
<td>( 4.3 \times 10^{14} )</td>
<td>54.6</td>
<td>0.0</td>
<td>[69]</td>
</tr>
<tr>
<td></td>
<td>( 8.6 \times 10^{14} )</td>
<td>27.5</td>
<td>1.5</td>
<td>[84]</td>
</tr>
</tbody>
</table>

**Table 2.3**: The rate constants of MPRM based on individual volatile constituents (Solomon et al. (1992)).
<table>
<thead>
<tr>
<th>Q-factor (dry basic)</th>
<th>ASTM Volatile % (dry basic)</th>
<th>Measured volatile mass loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6 mole% O₂</td>
<td>12 mole% O₂</td>
</tr>
<tr>
<td></td>
<td>Volatile mass loss % (dry)</td>
<td>Q-factor</td>
</tr>
<tr>
<td>Cerrejon</td>
<td>36.8</td>
<td>55</td>
</tr>
<tr>
<td>Blair Atholl</td>
<td>28.6</td>
<td>38</td>
</tr>
<tr>
<td>Ulan</td>
<td>31.0</td>
<td>42</td>
</tr>
<tr>
<td>PSOC 1445d Blue #1</td>
<td>43.5</td>
<td>51</td>
</tr>
<tr>
<td>PSOC 1451d Pittsburgh #8</td>
<td>32.6</td>
<td>49</td>
</tr>
<tr>
<td>PSOC 1488d Dietz</td>
<td>45.1</td>
<td>54</td>
</tr>
<tr>
<td>PSOC 1493d Illinois #6</td>
<td>36.4</td>
<td>51</td>
</tr>
<tr>
<td>PSOC 1502d Hiawatha</td>
<td>38.8</td>
<td>54</td>
</tr>
<tr>
<td>PSOC 1516d L.Kittaning</td>
<td>18.1</td>
<td>13</td>
</tr>
</tbody>
</table>

Table 2.4: Measured volatile mass loss and Q-factor in 6 and 12 mole-% oxygen environments (dry basic) (Jensen and Mitchell (1993)).

<table>
<thead>
<tr>
<th>Q-factor (daf basic)</th>
<th>ASTM Volatile % (daf basic)</th>
<th>Measured volatile mass loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6 mole% O₂</td>
<td>12 mole% O₂</td>
</tr>
<tr>
<td></td>
<td>Volatile mass loss % (daf)</td>
<td>Q-factor</td>
</tr>
<tr>
<td>Cerrejon</td>
<td>41.3</td>
<td>60.9</td>
</tr>
<tr>
<td>Blair Atholl</td>
<td>31.4</td>
<td>42.2</td>
</tr>
<tr>
<td>Ulan</td>
<td>37.3</td>
<td>48.9</td>
</tr>
<tr>
<td>PSOC 1445d Blue #1</td>
<td>45.7</td>
<td>52.9</td>
</tr>
<tr>
<td>PSOC 1451d Pittsburgh #8</td>
<td>38.4</td>
<td>54.6</td>
</tr>
<tr>
<td>PSOC 1488d Dietz</td>
<td>47.6</td>
<td>56.4</td>
</tr>
<tr>
<td>PSOC 1493d Illinois #6</td>
<td>43.1</td>
<td>57.4</td>
</tr>
<tr>
<td>PSOC 1502d Hiawatha</td>
<td>42.3</td>
<td>58.1</td>
</tr>
<tr>
<td>PSOC 1516d L.Kittaning</td>
<td>20.2</td>
<td>18.3</td>
</tr>
</tbody>
</table>

Table 2.5: Measured volatile mass loss and Q-factor in 6 and 12 mole-% oxygen environments (dry-ash-free (daf) basic) (Jensen and Mitchell (1993)).

2.3 Combustion of volatiles
Although the combustion properties of fuels have been studied empirically for many years, early numerical combustion modeling virtually ignored chemistry. In the last decade, numerical modelling has rapidly become an essential part of many combustion research and development programme, and there has been an accelerating evolution from the use of single-step empirical representations, to the use of lumped (overall) multistep models, and finally to the inclusion of full detailed chemical kinetic mechanisms to better simulate chemistry interactions (Dryer (1991), Westbrook and Dryer (1984)). For two- or three-dimensional geometry and turbulent combustion systems, full detailed chemical kinetic mechanisms with many reactions cannot currently be used because of the computational costs. A detailed chemical kinetic mechanism with few reactions (which some authors call quasi-global models) may be a best solution for accuracy and computational costs. Some global models and multistep reaction (quasi-global) models have been investigated and examined. More details of chemical kinetic mechanism in combustion systems can be found in Basevich (1987), Baulch et al. (1994), Glassman (1977), Warnatz (1984), Westbrokk and Dryer (1981b), Westbrook and Pitz (1984).

2.3.1 Composition of volatiles
The coal particles are assumed to be surrounded by air (premixed) and the volatiles mix with the air as they are released from the particles. If the gas temperature is sufficiently high, ignition will be spontaneous. A knowledge of the composition (mass fraction) of volatiles which evolve from coal particles is very important for the calculation of volatiles. Suuberg et al. (1979) have measured the composition of volatiles and of the formation kinetics of each product released from a lignite and a bituminous coal. They indicated that the lignite volatiles are dominated by CO, CO\textsubscript{2} and H\textsubscript{2}O, while the main volatiles from the bituminous coal are tar and light hydrocarbons. In general, pyrolysis water, carbon dioxide and tar evolve at low temperatures, whereas hydrocarbons, CO and hydrogen evolve at higher temperatures. In bituminous coal, tar constitutes 50-80\% of the released volatiles, the remaining volatiles consisting of hydrocarbon gases, water and oxides of carbon (Saxena (1990)). Several other investigations of the composition of volatiles have been made, e.g. Loison and Chauvin (1964), Serio et al. (1987). A review of investigations on product distribution is mentioned in Howard (1981).

According to Solomon et al. (1992), carbon dioxide (CO\textsubscript{2}), moisture (H\textsubscript{2}O), carbon monoxide (CO), hydrogen cyanide (HCN), ethylene (C\textsubscript{2}H\textsubscript{4}), methane (CH\textsubscript{4}), and hydrogen (H\textsubscript{2}) are the major gases (volatiles) from Illinois #6 coal. There are five active gases, CO, C\textsubscript{2}H\textsubscript{6}, CH\textsubscript{4}, H\textsubscript{2} and HCN, in volatiles, three of which (CO, CH\textsubscript{4} and H\textsubscript{2}) are most significant for coal combustion due to their high activities. Carbon monoxide is a most important gas, resulting partly from the pyrolysis, partly from the char oxidation. The following reactions and their rate constants may be used for calculating the combustion of volatiles. More details of these reactions are given in the relevant references. The original references of the multistep reactions are given in Miller et al. (1982), Westbrook and Dryer (1979), Westbrokk and Pitz (1984).

2.3.2 Global models
a) Oxidation of CH$_4$

The oxidation of a single species, e.g. CO, CH$_4$, H$_2$ etc., expressed by a single reaction is called global reaction. Many global reaction models for oxidations of CH$_4$ and CO have been studied. The global reaction for oxidation of CH$_4$ can be written as

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$  \hspace{1cm} (56)

The overall methane disappearance-rate expression in a turbulent-flow reactor at atmospheric pressure, over the temperature range 1100 - 1400 K, found by Dryer and Glassman (1973) is

$$\frac{d[CH_4]}{dt} = -1.58 \times 10^{13} \exp\left(\frac{-48400}{RT}\right) [CH_4]^{0.70} [O_2]^{0.80}$$  \hspace{1cm} (57)

Westbrook and Dryer (1981a) have developed one-step and two-step reaction mechanisms for hydrocarbon fuel (C$_n$H$_{2n+2}$, n = 1-10) using a numerical laminar flame model. They proposed a one-step reaction mechanism representing the oxidation of a conventional hydrocarbon fuel

$$Fuel + n_1O_2 \rightarrow n_2CO_2 + n_3H_2O$$  \hspace{1cm} (58)

and its rate constant

$$k_{ov} = AT^n \exp\left(\frac{-E_a}{RT}\right) [Fuel]^a [Oxidizer]^b$$  \hspace{1cm} (59)

The one-step reaction mechanism for hydrocarbon oxidation in a turbulent flow reactor can also be written (Westbrook and Dryer (1981a))

$$C_nH_m + \left(n + \frac{m}{4}\right)O_2 \rightarrow nCO_2 + \frac{m}{2}H_2O$$  \hspace{1cm} (60)

and a two-step reaction mechanism

$$C_nH_m + \left(\frac{n}{2} + \frac{m}{4}\right)O_2 \rightarrow nCO + \frac{m}{2}H_2O$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$  \hspace{1cm} (62)

The rate of the CO oxidation reaction is taken from Dryer and Glassman (1973). In order to reproduce both the proper heat of reaction and pressure dependence of the [CO]/[CO$_2$] equilibrium, a reverse reaction was defined for Eq.(62), with a rate

$$k_{CO_2\leftrightarrow CO + \frac{1}{2}O_2} = 5 \times 10^8 \exp(-40,000/RT) [CO_2]^{1.0}$$  \hspace{1cm} (63)
For methane air flame \((n = 1, m = 4)\), Eq.(61) becomes Eq.(56). The rate constants for methane air flame are shown in Table 2.6.

<table>
<thead>
<tr>
<th>Methane flame</th>
<th>A ([\text{mole/(cm}^3\text{s})])</th>
<th>(E_a) ([\text{kcal/mole}])</th>
<th>(a) [-]</th>
<th>(b) [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>One-step</td>
<td>1.3x10^8</td>
<td>48.4</td>
<td>-0.3</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>8.3x10^5</td>
<td>30.0</td>
<td>-0.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Two-step</td>
<td>2.8x10^9</td>
<td>48.4</td>
<td>-0.3</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>1.5x10^7</td>
<td>30.0</td>
<td>-0.3</td>
<td>1.3</td>
</tr>
</tbody>
</table>

**Table 2.6:** The rate constants for methane air flame (Westbrook and Dryer (1981a)).

According to Westbrook and Dryer (1981a), the two-step mechanism predicts flame speeds of methane-air (hydrocarbon-air) flames in close agreement with those predicted by the one-step model. However, the negative exponents can give problems in computation.

Williams et al. (1969) have studied the combustion of premixed methane-oxygen-nitrogen \((\text{CH}_4-\text{O}_2-\text{N}_2)\) mixtures in the range \(T = 1400-1800\ \text{K}\) and \(P = 0.3-1.1\ \text{atm}\) in a small \((2.9\ \text{cm}^3)\) conical reactor fed by a single-choked sonic-flow jet. The burning-rate for one-step reaction is

\[
\frac{d[\text{CH}_4]}{dt} = 5.3 \times 10^{12} \exp\left\{ \frac{57000}{RT_g} \right\} \left[ \text{CH}_4 \right] \left[ \text{O}_2 \right]^{0.5} \left[ \text{H}_2\text{O} \right]^{0.5} \quad (64)
\]

and for two-step reaction

\[
\frac{d[\text{CH}_4]}{dt} = 1.7 \times 10^{13} \exp\left\{ \frac{60000}{RT_g} \right\} \left[ \text{CH}_4 \right] \left[ \text{O}_2 \right]^{0.5} \left[ \text{H}_2\text{O} \right]^{0.5} \quad (65)
\]

\[
\frac{d[\text{CO}]}{dt} = 3.5 \times 10^6 \exp\left\{ \frac{20000}{RT_g} \right\} \left[ \text{CO} \right] \left[ \text{O}_2 \right]^{0.5} \left[ \text{H}_2\text{O} \right]^{0.5} \quad (66)
\]

**b) Oxidation of CO**

The global reaction for CO oxidation can be written

\[
\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \quad (67)
\]

Dryer and Glassman (1973) have studied carbon monoxide oxidation in the presence of water at atmospheric pressure, over the temperature range 1030 - 1230 K, and over water concentrations of 0.1% - 3.0%. With the linear least-square-fitting techniques, the rate
constant is found as

\[
\frac{d[CO]}{dt} = 3.98 \times 10^{14} \exp \left( \frac{-40000}{RT_g} \right) [CO] \left[ O_2 \right]^{0.25} \left[ H_2O \right]^{0.5}
\]

(68)

Howard et al. (1973) have developed a global model for CO oxidation from their flat methane-air flame experimental results and the previous data (Eq.(14)). The model is adequately correlated for the flame with the temperature range 840 - 2360 K.

\[
\frac{d[CO]}{dt} = 1.3 \times 10^{14} \exp \left( \frac{-30000}{RT_g} \right) [CO] \left[ O_2 \right]^{0.5} \left[ H_2O \right]^{0.5}
\]

(69)

Table 2.7 shows a review of overall rate parameters for CO oxidation for different flame types (experiments). The rate constants for CO oxidation as a function of temperature for 4 different flame types (stirred, jet stirred, turbulent flame and flat flame) are shown in Fig.2.5. There are large differences between them at T = 1000 K and 3000 K. Stirred reactor and flat flame have the same rate constants of CO oxidation at T = 1000 K, while the rate constants of CO oxidation in turbulent flame and jet stirred reactors have the same values. But at T = 3000 K, the rate constants in turbulent flame and flat flame are equal, and stirred and jet stirred reactors have almost the same values.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1280-1535</td>
<td>0.25 - 1</td>
<td>1.20x10^{11}</td>
<td>16.00</td>
<td>1</td>
<td>0.5</td>
<td>0.30</td>
<td>Stirred</td>
<td>[20,36]</td>
</tr>
<tr>
<td>1063-1593</td>
<td>1</td>
<td>1.80x10^{12}</td>
<td>28.30</td>
<td>1</td>
<td>0.5</td>
<td>0.25</td>
<td>Jet-stirred</td>
<td>[20,49]</td>
</tr>
<tr>
<td>970-1370</td>
<td>1</td>
<td>1.04x10^{12}/T^{2.5}</td>
<td>32.00</td>
<td>1</td>
<td>0.5</td>
<td>0.25</td>
<td>Laminar-flow</td>
<td>[20,46]</td>
</tr>
<tr>
<td>1030-1230</td>
<td>1</td>
<td>3.90x10^{14}</td>
<td>40.00</td>
<td>1</td>
<td>0.5</td>
<td>0.25</td>
<td>Turbulent flow</td>
<td>[20,34]</td>
</tr>
<tr>
<td>1750-2000</td>
<td></td>
<td>4.00x10^{13}</td>
<td>22.66</td>
<td>1</td>
<td>0.5</td>
<td>0.25</td>
<td>Flat-flame</td>
<td>[11,28]</td>
</tr>
<tr>
<td>840-2360</td>
<td>1</td>
<td>1.30x10^{14}</td>
<td>30.00</td>
<td>1</td>
<td>0.5</td>
<td>0.50</td>
<td>Jet-mixed</td>
<td>[37]</td>
</tr>
<tr>
<td>1400-1800</td>
<td>0.3-0.8</td>
<td>1.80x10^{13}</td>
<td>25.00</td>
<td>1</td>
<td>0.5</td>
<td>0.50</td>
<td>Flat-flame</td>
<td>[37]</td>
</tr>
<tr>
<td>1910-2400</td>
<td>1</td>
<td>2.70x10^{8}</td>
<td>27.00</td>
<td>1</td>
<td>0.2, 1**</td>
<td>0.00</td>
<td>Laminar Bunsen flame</td>
<td>[37,81]</td>
</tr>
<tr>
<td>1123-1298</td>
<td></td>
<td>1.50x10^{10}</td>
<td>23.6</td>
<td>1</td>
<td>0.5</td>
<td>0.25</td>
<td>Flat-flame</td>
<td></td>
</tr>
</tbody>
</table>
and the rate constants are

\[
\frac{d[C_aH_{2n+2}]}{dt} = -2.09 \times 10^{17} \exp\left(-\frac{49600}{RT_g}\right) \left[C_aH_{2n+2}\right]^{0.50} \left[O_2\right]^{1.07} \left[C_2H_4\right]^{0.4} \tag{78}
\]

\[
\frac{d[C_2H_4]}{dt} = -5.01 \times 10^{14} \exp\left(-\frac{50000}{RT_g}\right) \left[C_2H_4\right]^{0.90} \left[O_2\right]^{1.18} \left[C_2H_6\right]^{0.37} \tag{79}
\]

\[
\frac{d[CO]}{dt} = -3.98 \times 10^{14} \exp\left(-\frac{40000}{RT_g}\right) \left[CO\right]^{1.0} \left[O_2\right]^{0.25} \left[H_2O\right]^{0.5} \times S \tag{80}
\]

\[
\frac{d[H_2]}{dt} = -3.31 \times 10^{13} \exp\left(-\frac{41000}{RT_g}\right) \left[H_2\right]^{0.85} \left[O_2\right]^{1.42} \left[C_2H_4\right]^{0.56} \tag{81}
\]

where \(S = \max(1.0, 7.93 \exp\{-2.48\phi\})\), \(\phi\) is the initial equivalence ratio and \(S\) cannot take values greater than 1.

Several other multistep reaction models have been studied, e.g. four-step global reaction model for combustion of hydrocarbon (Jones and Lindstedt (1988)); multistep reactions models for CH4 oxidation, e.g. 7 reactions (Enikolopyan (1959)), 18 reactions (Rossberg (1956)), 23 reactions (Boni and Penner (1977)). Multistep reaction models for H2 oxidation have also been studied by others, e.g. 4 reactions (Baulch et al. (1972), Brown et al. (1974)).

Westbrook and Dryer (1981b) described the oxidation mechanism for carbon monoxide by 4 reactions (Eqs.(82)-(85)). The reaction with HO2 is usually negligible in comparison to the reaction with OH (Atri et al. (1977)). Several authors have used different reactions for calculating CO oxidation in methane flames, e.g. Smoot et al. (1976b), Tsatsaronis (1978) used two reactions (Eqs.(82) and (84)), and Jachimowski (1974) used two other reactions (Eqs.(83) and (84))

\[
CO + OH \rightarrow CO_2 + H \tag{82}
\]
\[
CO + O_2 \rightarrow CO_2 + O \tag{83}
\]
\[
CO + O + M \rightarrow CO_2 + M \tag{84}
\]
\[
CO + HO_2 \rightarrow CO_2 + OH \tag{85}
\]

Some rate constants for reaction CO+OH=CO2+H are shown in Table 2.8
### Table 2.8: The rate constants for reaction \( CO+OH=CO_2+H. \)

<table>
<thead>
<tr>
<th>( k_{CO+OH} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.6x10^{11} \exp{-1080/RT}</td>
<td>Singh and Sawyer (1971)</td>
</tr>
<tr>
<td>1.51x10^{7} T^{1.3} \exp{758/RT}</td>
<td>Baulch and Drysdale (1974)</td>
</tr>
<tr>
<td>3.1x10^{11} \exp{-596/RT}</td>
<td>Seery and Bowman (1970)</td>
</tr>
<tr>
<td>3.72x10^{11} \exp{-700/RT}</td>
<td>Browne et al. (1969)</td>
</tr>
<tr>
<td>4.8x10^{-12} \exp{-5700/RT}</td>
<td>Kondratiev. (1958)</td>
</tr>
<tr>
<td>2.32x10^{12} \exp{-5700/RT}</td>
<td>Vandooren et al. (1975)</td>
</tr>
</tbody>
</table>

#### 2.3.4 The kinetic reaction models used in the calculations

A global model with 3 reactions, 4 reduced models with 10 to 17 reactions, and an elementary model with 123 reactions were studied. The elementary model describes the oxidations of \( C_2H_6, CH_4, CO, H_2 \) and HCN, while other models describe the oxidations of CO, \( H_2 \) and \( CH_4 \). The rate constants for the \( i \) reactions are expressed as

\[
\frac{d[H_2]}{dt} = -3.31 \times 10^{13} \exp\left(-\frac{41000}{RT}\right) [H_2]^{0.85} [O_2]^{1.42}
\]  

The units of reaction rates, \( A_i \) and \( E_i \), are in moles, cubic centimetres, seconds, Kelvins and calories/mole.

**a) Global models (3 reactions):** Three reactions (Eqs.(87)-(89)) describing \( CH_4, CO \) and \( H_2 \) oxidations were chosen for the calculation of the volatiles evolving from coal

\[
CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O  \quad (87)
\]

\[
CO + \frac{1}{2}O_2 \rightarrow CO_2  \quad (88)
\]

\[
H_2 + \frac{1}{2}O_2 \rightarrow H_2O  \quad (89)
\]

The rate constant for \( CH_4 \) oxidation is taken from Dryer and Glassman (1973) (Eq.57), while the rate constant for CO oxidation is taken from Howard et al. (1973) (Eq.69). It is difficult to find a global reaction for \( H_2 \) oxidation. The rate constant used is taken from Hautman et al. (1981), where \([C_2H_4]^{0.56}\) is assumed to be unity.
**b) Reduced model 1 (10 reactions):** Ten reactions include a multistep model with 8 reactions describing H₂ oxidation, and two reactions for CO and CH₄ oxidations as in the global model.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A_i$</th>
<th>$\beta_i$</th>
<th>$E_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. H₂+OH=H₂O+H</td>
<td>1.17E9</td>
<td>1.30</td>
<td>3626.</td>
</tr>
<tr>
<td>2. H₂+O=H+OH</td>
<td>1.80E10</td>
<td>1.00</td>
<td>8826.</td>
</tr>
<tr>
<td>3. H+O₂=O+OH</td>
<td>5.13E16</td>
<td>-0.82</td>
<td>16507.</td>
</tr>
<tr>
<td>4. OH+O₂=O+H₂O</td>
<td>6.00E+8</td>
<td>1.30</td>
<td>0.</td>
</tr>
<tr>
<td>5. H+O+M=OH+M</td>
<td>6.20E16</td>
<td>-0.60</td>
<td>0.</td>
</tr>
<tr>
<td>6. O+O+M=O₂+M</td>
<td>7.50E23</td>
<td>0.00</td>
<td>0.</td>
</tr>
<tr>
<td>7. H+H+M=H₂+M</td>
<td>2.20E18</td>
<td>-1.00</td>
<td>0.</td>
</tr>
<tr>
<td>8. H+OH+M=H₂O+M</td>
<td>7.50E23</td>
<td>-2.60</td>
<td>0.</td>
</tr>
</tbody>
</table>

**c) Reduced model 2 (10 reactions):** The global (irreversible) reaction for CO oxidation in the reduced model 1 is replaced by a reversible reaction, i.e. CO reacts with OH (reaction 1). CH₄ oxidation is still calculated by a global reaction as in the global model. Reactions 1., 2., 3. and 4. have been examined in Howard et al. (1973).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A_i$</th>
<th>$\beta_i$</th>
<th>$E_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CO+OH=CO₂+H</td>
<td>1.51E7</td>
<td>1.30</td>
<td>-758.</td>
</tr>
<tr>
<td>2. H₂+OH=H₂O+H</td>
<td>1.17E9</td>
<td>1.30</td>
<td>3626.</td>
</tr>
<tr>
<td>3. H₂+O=H+OH</td>
<td>1.80E10</td>
<td>1.00</td>
<td>8826.</td>
</tr>
<tr>
<td>4. H+O₂=O+OH</td>
<td>5.13E16</td>
<td>-0.82</td>
<td>16507.</td>
</tr>
<tr>
<td>5. OH+O₂=O+H₂O</td>
<td>6.00E+8</td>
<td>1.30</td>
<td>0.</td>
</tr>
<tr>
<td>6. H+O+M=OH+M</td>
<td>6.20E16</td>
<td>-0.60</td>
<td>0.</td>
</tr>
<tr>
<td>7. O+O+M=O₂+M</td>
<td>7.50E23</td>
<td>0.00</td>
<td>0.</td>
</tr>
<tr>
<td>8. H+H+M=H₂+M</td>
<td>2.00E18</td>
<td>-1.00</td>
<td>0.</td>
</tr>
<tr>
<td>9. H+OH+M=H₂O+M</td>
<td>7.50E23</td>
<td>-2.60</td>
<td>0.</td>
</tr>
</tbody>
</table>

**d) Reduced model 3 (15 reactions):** CH₄ oxidation in reduced model 2 is calculated by 6 reversible reactions (reactions 10-15).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A_i$</th>
<th>$\beta_i$</th>
<th>$E_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CO+OH=CO₂+H</td>
<td>1.51E7</td>
<td>1.30</td>
<td>-758.</td>
</tr>
<tr>
<td>2. H₂+OH=H₂O+H</td>
<td>1.17E9</td>
<td>1.30</td>
<td>3626.</td>
</tr>
<tr>
<td>3. H₂+O=H+OH</td>
<td>1.80E10</td>
<td>1.00</td>
<td>8826.</td>
</tr>
<tr>
<td>4. H+O₂=O+OH</td>
<td>5.13E16</td>
<td>-0.82</td>
<td>16507.</td>
</tr>
<tr>
<td>5. OH+O₂=O+H₂O</td>
<td>6.00E+8</td>
<td>1.30</td>
<td>0.</td>
</tr>
<tr>
<td>6. H+O+M=OH+M</td>
<td>6.20E16</td>
<td>-0.60</td>
<td>0.</td>
</tr>
<tr>
<td>7. O+O+M=O₂+M</td>
<td>7.50E23</td>
<td>0.00</td>
<td>0.</td>
</tr>
<tr>
<td>8. H+H+M=H₂+M</td>
<td>2.20E18</td>
<td>-1.00</td>
<td>0.</td>
</tr>
<tr>
<td>9. H+OH+M=H₂O+M</td>
<td>7.50E23</td>
<td>-2.60</td>
<td>0.</td>
</tr>
</tbody>
</table>
H2O/20.0/
10. CH4+H=CH3+H2  2.20E4  3.00  8750.  (Kee et al. (1985))
11. CH4+O=CH3+OH  1.60E6  2.36  7400.  (Kee et al. (1985))
12. CH4+OH=CH3+H2O  1.60E6  2.10  2460.  (Kee et al. (1985))
13. CH3+H+M=CH4+M  8.00E26 -3.00  0.  (Kee et al. (1985))
14. CH3+O=CH2O+H  6.80E13  0.00  0.  (Kee et al. (1985))
15. CH3+OH=CH2O+H2  1.00E12  0.00  0.  (Kee et al. (1985))

**Reduced model 4 (17 reactions):** Reduced model 4 is reduced model 3 with two extra reactions for CO oxidation.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A_i</th>
<th>(\beta_i)</th>
<th>E_i</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CO+O+M=CO2+M</td>
<td>3.20E13</td>
<td>0.00</td>
<td>-4200. (Kee et al. (1985))</td>
</tr>
<tr>
<td>2. CO+OH=CO2+H</td>
<td>1.51E7</td>
<td>1.30</td>
<td>-758. (Baulch et al. (1974))</td>
</tr>
<tr>
<td>3. CO+O2=CO2+O</td>
<td>1.60E13</td>
<td>0.00</td>
<td>41000. (Kee et al. (1985))</td>
</tr>
<tr>
<td>4. H2+O=H2O+H</td>
<td>1.17E9</td>
<td>1.30</td>
<td>3626. (Kee et al. (1985))</td>
</tr>
<tr>
<td>5. H2+O=H2+OH</td>
<td>1.80E10</td>
<td>1.00</td>
<td>8826. (Kee et al. (1985))</td>
</tr>
<tr>
<td>6. H+O2=O2+OH</td>
<td>5.13E16</td>
<td>-0.82</td>
<td>16507. (Kee et al. (1985))</td>
</tr>
<tr>
<td>7. OH+OH=O+H2O</td>
<td>6.00E+8</td>
<td>1.30</td>
<td>0. (Kee et al. (1985))</td>
</tr>
<tr>
<td>8. H+O+M=OH+M</td>
<td>6.20E16</td>
<td>-0.60</td>
<td>0. (Kee et al. (1985))</td>
</tr>
</tbody>
</table>

**Elementary model (123 reactions):** C2H6, CH4, CO, H2 and HCN oxidations are calculated by 123 reversible reactions.

*** REACTION MECHANISM FOR C2H6 ***

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A_i</th>
<th>(\beta_i)</th>
<th>E_i</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. C2H6=CH3+CH3</td>
<td>2.24E19</td>
<td>-1.00</td>
<td>88310. (Westbrook and Pitz (1984))</td>
</tr>
<tr>
<td>2. C2H6+CH3=C2H5+CH4</td>
<td>0.55E0</td>
<td>4.00</td>
<td>8280. (Westbrook and Pitz (1984))</td>
</tr>
<tr>
<td>4. C2H6+OH=C2H5+H2O</td>
<td>8.71E9</td>
<td>1.05</td>
<td>1810. (Westbrook and Pitz (1984))</td>
</tr>
<tr>
<td>5. C2H6+O=C2H5+OH</td>
<td>2.51E13</td>
<td>0.00</td>
<td>1130. (Westbrook and Pitz (1984))</td>
</tr>
<tr>
<td>6. C2H4+M=C2H3+H+M</td>
<td>6.31E18</td>
<td>0.00</td>
<td>64700. (Westbrook and Pitz (1984))</td>
</tr>
<tr>
<td>7. C2H4+O=CH3+HCO</td>
<td>6.80E13</td>
<td>0.00</td>
<td>0. (Westbrook and Pitz (1984))</td>
</tr>
<tr>
<td>8. C2H4+O=CH2O+CH2</td>
<td>1.00E12</td>
<td>0.00</td>
<td>0. (Westbrook and Pitz (1984))</td>
</tr>
</tbody>
</table>
13. C2H4+H=C2H3+H2  1.51E7  2.00  6000.  (Westbrook and Pitz (1984))
14. C2H4+OH=C2H3+H2O  4.79E12  0.00  1230.  (Westbrook and Pitz (1984))
15. C2H4+OH=CH3+CH2O  2.00E12  0.00  31500. (Westbrook and Pitz (1984))
16. C2H3+M=C2H2+H+M  7.94E14  0.00  6000.  (Westbrook and Pitz (1984))
17. C2H3+O2=C2H2+HO2  1.00E12  0.00  10000. (Westbrook and Pitz (1984))
18. C2H2+M=C2H+H+M  1.00E14  0.00  114000. (Westbrook and Pitz (1984))
19. C2H2+O2=HCO+HCO  3.98E12  0.00  28000. (Westbrook and Pitz (1984))
20. C2H2+H=C2H+H2    2.00E14  0.00  19000. (Westbrook and Pitz (1984))
21. C2H2+OH=C2H+H2O  6.03E12  0.00  7000.  (Westbrook and Pitz (1984))
22. C2H2+OH=CH2CO+H  3.24E11  0.00  200.  (Westbrook and Pitz (1984))
23. C2H2+O=C2H+OH   3.23E15 -0.60  17000. (Westbrook and Pitz (1984))
24. C2H2+O=CH2+CO   6.76E13  0.00  4000.  (Westbrook and Pitz (1984))
25. C2H+O2=HCO+CO   1.00E13  0.00  7000.  (Westbrook and Pitz (1984))
26. C2H+O=CO+CH     5.01E13  0.00  0.  (Westbrook and Pitz (1984))

27. CH4+O2=CH3+HO2  7.90E13  0.00  56000.  (Kee et al. (1985))
28. CH4+H=CH3+H2   2.20E4  3.00  8750.  (Kee et al. (1985))
29. CH4+O=CH3+OH   1.60E6  2.36  7400.  (Kee et al. (1985))
30. CH4+OH=CH3+H2O  1.60E6  2.10  2460. (Kee et al. (1985))
31. CH3+H+M=CH4+M  8.00E26 -3.00  0.  (Kee et al. (1985))
32. CH3+O=CH2O+H   6.80E13  0.00  0.  (Kee et al. (1985))
33. CH3+OH=CH2O+H2  1.00E12  0.00  0.  (Kee et al. (1985))
34. CH3+OH=CH2+H2O  1.50E13  0.00  5000. (Kee et al. (1985))
35. CH3+H=CH2+H2   9.00E13  0.00  15100. (Kee et al. (1985))
36. CH2+H=CH+H2    1.40E19 -2.00  0.  (Kee et al. (1985))
37. CH2+OH=CH2O+H   2.50E13  0.00  0.  (Kee et al. (1985))
38. CH2+O=CH+H2O    4.50E13  0.00  3000. (Kee et al. (1985))
39. CH+O=CO+H      5.70E13  0.00  0.  (Kee et al. (1985))
40. CH+O2=HCO+O    3.30E13  0.00  0.  (Kee et al. (1985))
41. CH+OH=CO+H      3.00E13  0.00  0.  (Kee et al. (1985))
42. CH+CO2=CO2+H    3.40E12  0.00  690. (Kee et al. (1985))
43. CH2+CO2=CH2O+CO  1.10E11  0.00  100.  (Kee et al. (1985))
44. CH2+O=CO+H+H    3.00E13  0.00  0.  (Kee et al. (1985))
45. CH2+O=CO+H2     7.80E13  0.00  0.  (Kee et al. (1985))
46. CH2+O2=CO2+H+H  1.60E12  0.00  1000. (Kee et al. (1985))
47. CH2+O2=CH2O+O   5.00E13  0.00  9000. (Kee et al. (1985))
48. CH2+O2=CO2+H    6.90E11  0.00  500.  (Kee et al. (1985))
49. CH2+O2=CO+H2O  1.90E10  0.00 -1000. (Kee et al. (1985))
50. CH2+O2=CO+OH+H  8.60E10  0.00 -500. (Kee et al. (1985))
51. CH2+O2=HCO+OH   4.30E10  0.00 -500. (Kee et al. (1985))
52. CH2O+OH=HCO+H2O 3.43E9  1.18 -447. (Kee et al. (1985))
53. CH2O+H=HCO+H    2.19E8  1.77  3000. (Kee et al. (1985))
54. CH2O+M=HCO+H+M  3.31E16  0.00  81000. (Kee et al. (1985))
55. CH2O+O=HCO+OH   1.81E13  0.00  3082. (Kee et al. (1985))
56. HCO+OH=CO+H2O   5.00E12  0.00  0.  (Kee et al. (1985))
57. HCO+M=H+CO+M    1.60E14  0.00  14700. (Kee et al. (1985))
58. HCO+H=CO+H2     4.00E13  0.00  0.  (Kee et al. (1985))
59. HCO+O=CO2+H     1.00E13  0.00  0.  (Kee et al. (1985))
<table>
<thead>
<tr>
<th>Reactions</th>
<th>Rate Coefficient</th>
<th>Preexponential Factor</th>
<th>Activation Energy</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO + O₂ → HO₂ + CO</td>
<td>3.30E13</td>
<td>-0.40 0.</td>
<td>(Kee et al. 1985)</td>
<td></td>
</tr>
<tr>
<td>CO + O + M → CO₂ + M</td>
<td>3.20E13</td>
<td>0.00 -4200.</td>
<td>(Kee et al. 1985)</td>
<td></td>
</tr>
<tr>
<td>CO + OH → CO₂ + H</td>
<td>1.51E7</td>
<td>1.30 -758.</td>
<td>(Baulch and Drysdale 1974)</td>
<td></td>
</tr>
<tr>
<td>CO + O₂ → CO₂ + O</td>
<td>1.60E13</td>
<td>0.00 0.41000.</td>
<td>(Kee et al. 1985)</td>
<td></td>
</tr>
<tr>
<td>CO + HO₂ → CO₂ + OH</td>
<td>5.80E13</td>
<td>0.00 22934.</td>
<td>(Kee et al. 1985)</td>
<td></td>
</tr>
<tr>
<td>H₂ + O₂ → OH + OH</td>
<td>1.70E13</td>
<td>0.00 47780.</td>
<td>(Kee et al. 1985)</td>
<td></td>
</tr>
<tr>
<td>H₂ + OH → H₂O + H</td>
<td>1.17E9</td>
<td>1.30 3626.</td>
<td>(Dixon-Lewis 1968)</td>
<td></td>
</tr>
<tr>
<td>H + O₂ → H₂ + O₂</td>
<td>5.13E16</td>
<td>-0.82 16507.</td>
<td>(Kee et al. 1985)</td>
<td></td>
</tr>
<tr>
<td>H + O₂ + M → HO₂ + M</td>
<td>2.10E18</td>
<td>-1.00 0.</td>
<td>(Slack 1977)</td>
<td></td>
</tr>
<tr>
<td>H₂O → 2H₂O</td>
<td>2.23E12</td>
<td>0.50 92600.</td>
<td>(Kee et al. 1985)</td>
<td></td>
</tr>
<tr>
<td>H + H + H₂ → H₂ + H₂</td>
<td>9.20E16</td>
<td>-0.60 0.</td>
<td>(Kee et al. 1985)</td>
<td></td>
</tr>
<tr>
<td>H + H + H₂O → H₂ + H₂O</td>
<td>6.00E19</td>
<td>-1.25 0.</td>
<td>(Kee et al. 1985)</td>
<td></td>
</tr>
<tr>
<td>H + O + CO₂ → H₂ + CO₂</td>
<td>5.49E20</td>
<td>-2.00 0.</td>
<td>(Kee et al. 1985)</td>
<td></td>
</tr>
<tr>
<td>H + OH + M → H₂O + M</td>
<td>7.50E23</td>
<td>-2.60 0.</td>
<td>(Glarborg et al. 1992)</td>
<td></td>
</tr>
<tr>
<td>H₂O → H₂O + H₂</td>
<td>6.20E16</td>
<td>-0.60 0.</td>
<td>(Dixon-Lewis 1968)</td>
<td></td>
</tr>
<tr>
<td>H + HO₂ → H₂ + O₂</td>
<td>2.50E13</td>
<td>0.00 700.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>H₂O + H₂O → H₂O₂ + H₂O</td>
<td>2.00E12</td>
<td>0.00 0.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>H₂O + H + OH → H₂O + OH</td>
<td>2.50E14</td>
<td>0.00 1900.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>H₂O₂ + M → OH + OH + M</td>
<td>1.30E17</td>
<td>0.00 45500.</td>
<td>(Baulch et al. 1972)</td>
<td></td>
</tr>
<tr>
<td>H₂O₂ + H → HO₂ + H₂</td>
<td>1.60E12</td>
<td>0.00 3750.</td>
<td>(Baulch et al. 1972)</td>
<td></td>
</tr>
<tr>
<td>H₂O₂ + OH → H₂O + HO₂</td>
<td>1.00E13</td>
<td>0.00 1800.</td>
<td>(Baulch et al. 1972)</td>
<td></td>
</tr>
<tr>
<td>O + HO₂ → O₂ + OH</td>
<td>5.00E13</td>
<td>0.00 0.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>O + HO₂ + M → H + HO₂ + M</td>
<td>5.00E13</td>
<td>0.00 0.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>O + HO₂ = O₂ + H</td>
<td>4.80E13</td>
<td>0.00 1000.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>OH + HO₂ → H₂O₂</td>
<td>6.00E13</td>
<td>0.00 0.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
</tbody>
</table>

*** REACTION MECHANISM FOR HCN ***

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Rate Coefficient</th>
<th>Preexponential Factor</th>
<th>Activation Energy</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN + OH → CN + H₂O</td>
<td>4.40E12</td>
<td>0.00 9000.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>HCN + O → NCO + H</td>
<td>1.21E4</td>
<td>2.64 4980.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>HCN + O → NH + CO</td>
<td>5.17E3</td>
<td>2.64 4980.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>HCN + O → CN + OH</td>
<td>2.70E9</td>
<td>1.58 26600.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>CN + H₂ → HCN + H</td>
<td>5.45E11</td>
<td>0.70 4885.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>CN + O → CO + N</td>
<td>1.80E13</td>
<td>0.00 0.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>CN + O₂ → NCO + O</td>
<td>5.60E12</td>
<td>0.00 0.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>CN + O → NCO + H</td>
<td>5.00E13</td>
<td>0.00 0.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>NCO + H → NH + CO</td>
<td>5.00E13</td>
<td>0.00 0.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>NCO + O → NO + CO</td>
<td>3.00E13</td>
<td>0.00 0.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>NCO + N → N₂ + CO</td>
<td>2.00E13</td>
<td>0.00 0.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>NCO + OH → NO + CO + H</td>
<td>1.00E13</td>
<td>0.00 0.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>NCO + O → NO + CO + H</td>
<td>3.00E16</td>
<td>-0.50 48000.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>NCO + NO → N₂O + CO</td>
<td>1.90E13</td>
<td>0.00 0.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>NCO + H₂ → HNCO + H</td>
<td>8.58E12</td>
<td>0.00 9000.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>HNCO + H = NH₂ + CO</td>
<td>2.00E13</td>
<td>0.00 3000.</td>
<td>(Miller et al. 1984)</td>
<td></td>
</tr>
<tr>
<td>NH + O₂ → HNO + O</td>
<td>1.00E7</td>
<td>0.00 12000.</td>
<td>(Miller et al. 1983)</td>
<td></td>
</tr>
<tr>
<td>NH + O₂ → NO + O₂</td>
<td>1.40E11</td>
<td>0.00 2000.</td>
<td>(Miller et al. 1983)</td>
<td></td>
</tr>
<tr>
<td>NH + NO → N₂O + H</td>
<td>4.33E14</td>
<td>-0.50 0.</td>
<td>(Miller et al. 1983)</td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>Rate Constant</td>
<td>Energy</td>
<td>Temperature</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>---------------</td>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>N2O + H = N2 + OH</td>
<td>7.60E13</td>
<td>0.00</td>
<td>15200</td>
<td></td>
</tr>
<tr>
<td>NH + OH = HNO + H</td>
<td>2.00E13</td>
<td>0.00</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>NH + OH = N + H2O</td>
<td>5.00E11</td>
<td>0.50</td>
<td>2000</td>
<td></td>
</tr>
<tr>
<td>NH + N = N2 + H</td>
<td>3.00E13</td>
<td>0.00</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>NH + H = N + H2</td>
<td>3.00E13</td>
<td>0.00</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>NH2 + O = HNO + H</td>
<td>6.63E14</td>
<td>-0.50</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>NH2 + O = NH + OH</td>
<td>6.75E12</td>
<td>0.00</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>NH2 + OH = NH + H2O</td>
<td>4.50E12</td>
<td>0.00</td>
<td>2200</td>
<td></td>
</tr>
<tr>
<td>NH2 + H = N2 + H2</td>
<td>6.92E13</td>
<td>0.00</td>
<td>3650</td>
<td></td>
</tr>
<tr>
<td>NH2 + NO = NNH + OH</td>
<td>8.82E15</td>
<td>-1.25</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>NH2 + NO = N2 + H2O</td>
<td>3.78E15</td>
<td>-1.25</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>NNH + M = N2 + H + M</td>
<td>2.00E14</td>
<td>0.00</td>
<td>20000</td>
<td></td>
</tr>
<tr>
<td>NNH + NO = N2 + HNO</td>
<td>5.00E13</td>
<td>0.00</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>NNH + H = N2 + H2</td>
<td>3.70E13</td>
<td>0.00</td>
<td>3000</td>
<td></td>
</tr>
<tr>
<td>HNO + M = H + NO + M</td>
<td>1.50E16</td>
<td>0.00</td>
<td>48680</td>
<td></td>
</tr>
<tr>
<td>HNO + OH = NO + H2O</td>
<td>3.60E13</td>
<td>0.00</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>HNO + H = H2 + NO</td>
<td>5.00E12</td>
<td>0.00</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>N + NO = N2 + O</td>
<td>3.27E12</td>
<td>0.30</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>N + O2 = NO + O</td>
<td>6.40E9</td>
<td>1.00</td>
<td>6280</td>
<td></td>
</tr>
<tr>
<td>N + OH = NO + H</td>
<td>3.80E13</td>
<td>0.00</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>
2.4 Combustion of coal char

The overall reaction process involves several steps in sequence: transport of oxygen or other reactant gas to the surface of the particle, reaction with the surface, and transport of products away. Oxygen is transported to the surface and products are transported away by molecular diffusion, owing to concentration gradients between the surface and the free gas stream. The most important reactions on the surface of particles may be (Field et al. (1967))

\[
\begin{align*}
C_f + O_2 & \rightarrow CO_2 \\
C_f + \frac{1}{2}O_2 & \rightarrow CO \\
C_f + O & \rightarrow CO \\
C_f + CO_2 & \rightarrow 2CO \\
C_f + H_2O & \rightarrow CO + H_2
\end{align*}
\]

\( C_f \) is the fixed carbon of coal char. Depending on the nature of products formed at the particle surface, several char oxidation models are proposed: single-film model, double-film model and continuous-film model.

- **Single-film model**: (Caram and Amundson (1977), Laurendeau (1978), Mitchell and Madsen (1986)) The particle is consumed via reactions with oxygen and no reaction occurs in the boundary layer. CO and CO\(_2\) are the heterogeneous products and CO reacts with oxygen after it has been transported to the free stream. If the particle temperature is above 1273 K, the main product of the reaction is CO (Arthur (1951)). The single-film model is applicable for particle diameters less than 100 µm (Ayling and Smith (1972)).

- **Double-film model**: (Caram and Amundson (1977), Laurendeau (1978), Mitchell and Madsen (1986)) Oxygen from the gas phase diffuses to the surface of the particle and reacts with the fixed carbon of the coal to form carbon monoxide (CO) and carbon dioxide (CO\(_2\)) (Eqs.(1) and (2)). One-half of the CO\(_2\) formed in the reaction zone surrounding the particles diffuses back to the particle surface and reacts with the fixed carbon to form carbon monoxide (Eq.(4)) and the other one-half diffuses out into the main air stream. The CO formed diffuses outwards into the air stream where it reacts with the incoming oxygen to form carbon dioxide in the gas phase. The double film is adequate for particle diameters greater than 1 mm (Wicke and Wurzbacher (1962)).

- **Continuous-film model**: (Caram and Amundson (1977), Laurendeau (1978), Mitchell and Madsen (1986)) This model is important for particle sizes between 100 and 1000 µm. The oxygen of air comes in contact with the carbon of the particle, and both CO and CO\(_2\) are produced. However, if the temperature is greater than about 923 K (the ignition temperature of CO), the CO burns anywhere within the boundary layer depending on particle size. If the particle temperature is above 1373 K, CO\(_2\) is reduced to CO on the particle surface.
In this work, the burning of coal char is described by the single-film model, i.e. CO and CO$_2$ are the heterogeneous products and CO reacts with oxygen after it has been transported to the free stream. Two models are used for calculations. The first one, called char oxidation model 1, is described in Mitchell (1988) and the second, or simple one, called char oxidation model 2, is described in Field et al. (1967). It is called a simple model because the apparent reaction order equals unity. We must distinguish between two different meanings for the word "model" in this subsection: "model" in the single-film model, double-film model and continuous-film model indicates the products and how they are formed on the surface of particle; "model" in e.g. model of Field et al. (1967) and Mitchell (1988) indicates the speed at which the particles can burn.

2.4.1 Char oxidation model 1 (Mitchell's model): (Mitchell (1988))

The overall particle burning rate per unit external surface area is expressed as

\[
q = \frac{K_d}{\gamma} \ln \left( \frac{1 - \frac{\gamma P_s}{P}}{1 - \frac{\gamma P_g}{P}} \right)
\]  

(96)

\(P\) is the total pressure, \(P_s\) is the oxygen partial pressure at the particle surface, \(P_g\) is the oxygen partial pressure in the gas phase and \(K_d\) is the mass transfer (diffusive) coefficient, given by

\[
K_d = \frac{P M_c D_{ox}(Sh)}{d_p R' T_m \nu_o}
\]  

(97)

\(\gamma = (\psi-1)/(\psi+1)\) is the change in volume during reaction referred to unit volume of oxygen, \(\psi = 1/(1+CO/CO_2)\) is the fraction of carbon converted to CO$_2$ at the particle surface, \(\nu_o = 0.5(1+\psi)\) is the stoichiometric oxygen coefficient for reaction at the particle surface, \(Sh\) is the Sherwood number, \(R' = 82.06\) atm cm$^3$ mole$^{-1}$ K$^{-1}\) is the gas constant, \(M_c\) is the molecular weight of carbon, and \(D_{ox}\) is the diffusion coefficient of oxygen. It is defined as (Field et al. (1967))

\[
D_{ox} = D_{ox,0} \left( \frac{T_m}{T_0} \right)^{1.75}
\]  

(98)

\(D_{ox,0} = 0.207\text{cm}^2/\text{s}\) for O$_2$-N$_2$ at 300 K.

The Sherwood number, \(Sh\), is calculated as
\[ Sh = \frac{\lambda d_p}{D_{ki}} = 2.0 + 0.65 \left( Re^{\frac{1}{3}} (Sc)^{\frac{1}{3}} \right) \]  

(99)

Sc = \frac{v}{D_{ki}} \text{ is the Schmidt number; } Sh = 2 \text{ for velocities of gas and particles are equal.}

The apparent density and diameter of a burning char particle are defined

\[ \frac{\rho_p}{\rho_{p,0}} = \left( \frac{m_p}{m_{p,0}} \right)^a \]  

(100)

and

\[ \frac{d_p}{d_{p,0}} = \left( \frac{m_p}{m_{p,0}} \right)^b \]  

(101)

The subscript 0 denotes the initial values. According to Mitchell (1988), for spherical particles, \( a + 3b = 1.0 \). For constant density burning, \( a = 0 \) and for constant diameter burning \( a = 1.0 \). For values of \( a \) between 0 and 1, both the size and density of a particle decrease with burnoff. Further details of \( a \) and \( b \) can be found in Mitchell (1988), Smith (1971a,b).

In terms of an apparent chemical reaction rate coefficient, \( K_s \), and an apparent reaction order with respect to the oxygen partial pressure, \( n \), the overall particle burning rate is expressed as

\[ q = K_s P_s^n \]  

(102)

\( K_s \) is the apparent chemical reaction rate coefficient, written as

\[ K_s = A_s \exp \left( -\frac{E_a}{RT_p} \right) \]  

(103)

Inserting \( P_s \) in Eq.(102) into Eq.(96), yields

\[ \frac{\gamma}{P} \left\{ \frac{q}{K_s} \right\}^{\frac{1}{n}} + \left( 1 - \frac{P_g}{P} \right) \exp \left( \frac{\gamma}{K_d} q \right) - 1 = 0 \]  

(104)

or

\[ F(q) = \frac{\gamma}{P} \left\{ \frac{q}{K_s} \right\}^{\frac{1}{n}} + \left( 1 - \frac{P_g}{P} \right) \exp \left( \frac{\gamma}{K_d} q \right) - 1 = 0 \]  

(105)

Differentiating Eq.(104), yields
Eq. (105) and (106) are nonlinear algebraic equations which can be solved by the Newton-Raphson method. The Newton-Raphson method is implemented by executing the following sequence of steps

1. Guess $q^0$
2. Setting $q^0 = q^n$ into Eqs. (105) and (106) then calculating $q^1$ ($q^1 \approx q^{n+1}$ in Eq. (107))
3. Setting $q^1 = q^n$ into Eqs. (105) and (106) then calculating $q^2$ ($q^2 \approx q^{n+1}$ in Eq. (107)), etc. until $q^{n+1} - q^n < \text{eps}$ (e.g. $\text{eps} = 1.0E-10$).

\[
q^{n+1} = q^n - \left( \frac{\partial F(q)}{\partial q} \right)_{q^n}^{-1} \cdot F(q^n)
\]  \hspace{1cm} (107)

The combustion parameters for Mitchell’s char oxidation model are shown in Table 2.9. The combustion parameters of Mitchell’s model are different for different coal types.

<table>
<thead>
<tr>
<th>Coal type</th>
<th>Pre-exponential factor [g cm(^{-2}) s(^{-1}) atm(^{-n})]</th>
<th>Activation energy [cal/mol]</th>
<th>Apparent order of reaction [-]</th>
<th>Particle diameter [µm]</th>
<th>O(_2)-environment [%]</th>
<th>Temperature [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illinois #6</td>
<td>6907.0</td>
<td>34133.0</td>
<td>0.17</td>
<td>13.0</td>
<td>0.1-0.5</td>
<td>1700-2200</td>
</tr>
<tr>
<td></td>
<td>1.72</td>
<td>16790.0</td>
<td>0.25</td>
<td>75-125</td>
<td>6 and 12</td>
<td>1550-1700</td>
</tr>
<tr>
<td></td>
<td>22.4</td>
<td>22500.0</td>
<td>0.50</td>
<td>106-125</td>
<td>6 and 12</td>
<td>1535-1700</td>
</tr>
<tr>
<td>Pittsburgh #8</td>
<td>4564.0</td>
<td>33967.0</td>
<td>0.17</td>
<td>3.3</td>
<td>0.1-0.5</td>
<td>1700-2200</td>
</tr>
<tr>
<td></td>
<td>664.0</td>
<td>29194.0</td>
<td>0.17</td>
<td>14.9</td>
<td>0.1-0.5</td>
<td>1700-2200</td>
</tr>
<tr>
<td></td>
<td>29.0</td>
<td>24000.0</td>
<td>0.5</td>
<td>75-125</td>
<td>6 and 12</td>
<td>1535-1700</td>
</tr>
<tr>
<td></td>
<td>7.21</td>
<td>19310.0</td>
<td>0.5</td>
<td>106-125</td>
<td>6 and 12</td>
<td>1550-1700</td>
</tr>
<tr>
<td>Cerrejon</td>
<td>9.0</td>
<td>24100.0</td>
<td>0.1</td>
<td>106-125</td>
<td>6 and 12</td>
<td>1535-1700</td>
</tr>
<tr>
<td>Middleburgh</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ulan</td>
<td>49.4</td>
<td>29000.0</td>
<td>0.2</td>
<td>106-125</td>
<td>6 and 12</td>
<td>1535-1700</td>
</tr>
<tr>
<td>Blair Atholl</td>
<td>11.1</td>
<td>24700.0</td>
<td>0.1</td>
<td>106-125</td>
<td>6 and 12</td>
<td>1535-1700</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[50]</td>
</tr>
<tr>
<td>[58]</td>
</tr>
<tr>
<td>[40]</td>
</tr>
<tr>
<td>[50]</td>
</tr>
<tr>
<td>[50]</td>
</tr>
<tr>
<td>[40]</td>
</tr>
<tr>
<td>[58]</td>
</tr>
<tr>
<td>[40]</td>
</tr>
<tr>
<td>[40]</td>
</tr>
<tr>
<td>[40]</td>
</tr>
</tbody>
</table>

Table 2.9: Summary of char combustion parameters.

2.4.2 Char oxidation model 2 (Field et al. (1967))
The rate of reaction of carbon with oxygen can be expressed as

\[ q = K_s p_s \]  
(108)

where \( q \) is the rate of consumption of carbon (g/(cm\(^2\) s)), \( K_s \) is the surface reaction rate coefficient (g/(cm\(^2\) s atm)), and \( p_s \) is the oxygen partial pressure at the surface (atm).

The surface reaction rate coefficient is independent of the oxygen concentration, and depends on the surface temperature as well as on the fuel type. \( K_d \) is defined as

\[ K_s = A_a \exp\left(-\frac{E_a}{R T_p}\right) \]  
(109)

where \( T_p \) is the particle temperature at the surface, \( A_a = 8710 \, \text{g/cm}^2 \), \( E_a = 35700 \, \text{cal/mole} \) are the empirical values. \( K_s \) is discussed in Field et al. (1967).

In the boundary layer, assumed that the oxygen is conserved, i.e. oxygen is transport through a imaginary surface at any radius and is equal to the rate of oxygen transported to the particle surface.

\[ 4 \pi r^2 G(r_0) = 4 \pi r^2 G(r) \]  
(110)

where \( r \) is the radial distance from the centre of the particle, \( r_0 \) is the radius of the particle, and \( G(r) \) is the flux of oxygen at radius \( r \).

The flux of oxygen is given by the diffusional transport equation

\[ G(r) = -\frac{D_{ox} M_o}{R' T_g} \frac{dP}{dr} \]  
(111)

\( D_{ox} \) is the diffusion coefficient of oxygen in the gas, \( M_o \) is the molecular weight of oxygen, \( R' \) is the gas constant (\( = 82.06 \, \text{atm cm}^3/(\text{mole K}) \)), \( T \) is the gas temperature, and \( P \) is partial pressure of oxygen.

Substituting for the oxygen flux in Eq.(110) yields

\[ r_0^2 G(r_0) = \frac{D_{ox} M_o}{R' T_g} r^2 \frac{dP}{dr} \]  
(112)
or

\[ r_0^2 G(r_0) \frac{R' T_g}{D_{ox} M_o r^2} \frac{l}{dP}{dr} = \frac{dP}{dr} \]  
(113)
Assuming that the variation of temperature can be disregarded, integrating Eq.(113) between any radius \( r \) and the particle surface \( r_0 \), yields

\[
r_0 G(r_0) \frac{R'T_m}{D_{oc} M_o} \left( 1 - \frac{r_0}{r} \right) = P(r) - P(r_0)
\]

(114)

Far from the particle, \( r_0/r \) approaches zero and the oxygen concentration tends to be the value in the free stream, i.e.

\[
r_0 G(r_0) \frac{R'T_m}{D_{oc} M_o} = P_g - P_s
\]

(115)

\( P_g \) and \( P_s \) are the oxygen partial pressures in the free stream and at the particle surface, respectively.

This equation gives the rate of transport of oxygen to the particle surface in terms of the concentration of oxygen in the free stream and at the surface. The ratio of carbon consumed to oxygen transported to the surface depends on the product which is transported away. In general, the relation may be written

\[
\frac{q}{M_c} = \frac{\frac{\varphi}{G(r_0)}}{M_o}
\]

(116)

or

\[
q = \frac{M_c \varphi G(r_0)}{M_o}
\]

(117)

where \( q \) is the rate of consumption of carbon \( (g/(cm^2 \text{ s})) \), \( \varphi \) is the mechanism factor which takes the values 1 when \( \text{CO}_2 \) is the sole heterogeneous product and 2 when \( \text{CO} \) is the sole product.

Combining Eqs.(115) and (117) yields

\[
q = \frac{M_c \varphi D_{oc}}{r_0 R'T_m} (P_g - P_s) = K_d (P_g - P_s)
\]

(118)

where

\[
K_d = \frac{M_c \varphi D_{oc}}{r_0 R'T_m}
\]

(119)

\( K_d \) is the diffusional reaction rate coefficient. It depends on the particle diameter, the mechanism factor and the mean temperature, but is completely independent of fuel type. Eq.(97) is similar to Eq.(119) with \( P = 1 \text{ atm}, \ Sh = 2.0 \) and \( v_0 = 1/\varphi \). In all calculations, \( K_d \) is taken from Eq.(97).
The mean temperature can be calculated as

$$T_m = \frac{1}{2}(T_s + T_p)$$

(120)

If the surface reaction rate coefficient is sufficiently high, the oxygen partial pressure at the surface may be small compared with the value in the free stream. The reaction is then said to be diffusion-controlled.

Combining Eqs.(108) and (118), we obtain

$$q = \frac{p_g}{I + \frac{I}{K_s + K_d}}$$

(121)

This equation is used to calculate the rate of consumption of carbon. $K_s$ and $K_d$ are described in Eqs.(109) and (119), respectively.

2.4.3 Formation of CO and CO$_2$

The model allows for both CO and CO$_2$ formation at the particle surface, but assumes that no reaction occurs in the boundary layer surrounding the particle. According to Mitchell [1988], the ratio CO/CO$_2$ increases with increasing temperature. Formation of CO and CO$_2$ can be expressed as

$$\frac{(\text{moles CO})}{(\text{moles CO}_2)} = A_{CO} \exp\left(-\frac{E_{CO}}{RT_p}\right)$$

(122)

where $A_{CO}$ and $E_{CO}$ are the pre-exponential factor and activation energy for formation of CO and CO$_2$, respectively. The empirical constants of $A_{CO}$ and $E_{CO}$ are shown in Table 2.10. In Jensen and Mitchell (1993), $A_{CO}$ and $E_{CO}$ are different for different coal types.
Table 2.10: Summary of ratio of CO/CO₂ product. *: CO is the sole heterogeneous reaction product.

The ratio of CO to CO₂ as a function of the inverse temperature (1/T) is shown in Fig.2.6, and the fraction of carbon converted to CO₂ at the particle surface, ψ, as function of temperature is shown in Figs.2.7 and 2.8. The CO/CO₂ and ψ profiles calculated by Arthur's and Rossberg's constants are nearly the same, while the CO/CO₂ and ψ profiles using Mitchell's constant are quite different.

Figure 2.6: CO/CO₂ as function of 1/T (T: particle temperature).
Figure 2.7: Mole fraction of CO$_2$ as function of $1/T$ (T: particle temperature).

Figure 2.8: Mole fraction of CO$_2$ as function of $T$ (T: particle temperature).
3 RESULTS AND DISCUSSIONS

Numerous mathematical models for coal reaction process, including devolatilization, char oxidation, gas phase oxidation, and gas-particle interchange have been proposed. However, the choice of single subprocess, e.g. devolatilization, char oxidation, gas phase oxidation, is very difficult. In this work, two devolatilization models, Multiple Parallel Reaction Model (MPRM) and Distributed Activation Energy Model (DAEM), were used for decomposition kinetics. Six sets of multistep reaction models were used for calculation of combustion of volatiles (CO, HCN, C2H6, CH4 and H2). The combustion of coal char was described by single film model with two different "reaction rates" called Mitchell's model (model 1) and model of Field et al. (1967) (model 2). The influence of radiative heat transfer between particles and radiation of hot particles to the cold environment were also examined.

The measured gas temperatures were used to compute reaction rates. The gas temperatures are known (measured) so that they could not influence the kinetic (homogeneous) reactions. The temperature difference between the particles and the gas depends on the rate of heat generation (char oxidation) and on the rate at which the particle dissipates heat by conduction (convection if there is slip velocity between gas and particles) and radiation. The heat generation depends on the amount of consumed fixed carbon (over all particle burning rate) to form carbon monoxide and carbon dioxide. Without the char oxidation model in the calculations, the cold particles are only heated by the hot gas (conduction) and hot particles (radiation) and give simultaneously heat to the cold environment by radiation. With the char oxidation model, the cold particles are heated by hot gas and hot particle. At the exit plan of the burner (burner outlet), they begin to release volatiles and ignite (char burning). The particles now are hotter than the surrounding gas, they heat the gas by conduction and heat the cold particles at both ends of the flame by radiation.

Illinois #6 and Pittsburgh #8 coals were chosen for testing due to their many available data. Major species profiles (CO2, O2, CO, CH4 and H2) were compared with the experimental data. All calculated mole fractions of species are converted to "dry basic" data. The unit in all concentration figures is written in mole fraction with the 6 major gases N2, CO2, O2, CO, CH4 and H2. The gas temperature profile (GTP) and the particle temperature profile (PTP) from calculations and experiment were also shown. The "calculated" gas temperatures have the same values as the experimental data, and the particle temperatures were calculated by Eq.(2). The coordinate with negative sign means that the distance before burner outlet. The oxidizer is the dry air with mole fractions as follow: %N2 = 78.09, %O2 = 20.95,, %CO2 = 0.03, and %AR = 0.93. The amount of volatiles in calculation were taken as the volatile matters from the proximate analysis times with the Q-factor, which were taken from Jensen and Mitchell (1993) (1.385 for Illinois #6 coal and 1.50 for Pittsburgh #8 coal). Except for the cases called "New ultimate analysis", all analysis values (both proximate and ultimate values) of Illinois #6 and Pittsburgh #8 coals used in the calculations were taken from column (2) of Table A3 (APP.A1). The used analysis values for case "New ultimate analysis" were taken from column (3) of Table A3 (only for Illinois
The calculated residence time of coal particles in Illinois #6 coal air flame is shown in Fig. 3.1, and the calculated gas (particle) velocity profile is shown in Fig. 3.2. The residence time of coal particles from the burner outlet (x = 0.0 cm) to the end of the calculated domain (x = 3.0 cm) is about 0.046 sec. After the burner outlet, the velocity of gas (particle) increases very fast due to the hot gas (low gas mass density).

Table 3.1 shows the compositions of combustion products for six sets of kinetic reaction models and the total mole fractions of major species. The total mole fractions of minor products vary from 8.3% for using global model to 18.0% for using elementary model (by difference with the total mole fraction of major products in Table 3.1). Only CO₂, O₂, CO, CH₄ and H₂ concentration (mole fraction) profiles are shown and compared with the experimental data.
<table>
<thead>
<tr>
<th>Volatile combustion models</th>
<th>Number of reactions</th>
<th>Composition of combustion products</th>
<th>Sum of mole fractions of O&lt;sub&gt;2&lt;/sub&gt;, H&lt;sub&gt;2&lt;/sub&gt;, CO&lt;sub&gt;2&lt;/sub&gt;, CO, N&lt;sub&gt;2&lt;/sub&gt;, CH&lt;sub&gt;4&lt;/sub&gt; (major products)</th>
<th>Without char oxidation model (%)</th>
<th>With char oxidation model (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global Model</td>
<td>3</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O, O&lt;sub&gt;2&lt;/sub&gt;, H&lt;sub&gt;2&lt;/sub&gt;, CO&lt;sub&gt;2&lt;/sub&gt;, CO, C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;, HCN, Ar, N&lt;sub&gt;2&lt;/sub&gt;, CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>91.69</td>
<td>91.90</td>
<td></td>
</tr>
<tr>
<td>Reduced Model 1</td>
<td>10</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O, O&lt;sub&gt;2&lt;/sub&gt;, O, OH, H&lt;sub&gt;2&lt;/sub&gt;, H, CO&lt;sub&gt;2&lt;/sub&gt;, CO, C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;, HCN, Ar, N&lt;sub&gt;2&lt;/sub&gt;, CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>85.96</td>
<td>85.94</td>
<td></td>
</tr>
<tr>
<td>Reduced Model 2</td>
<td>10</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O, O&lt;sub&gt;2&lt;/sub&gt;, O, OH, H&lt;sub&gt;2&lt;/sub&gt;, H, CO&lt;sub&gt;2&lt;/sub&gt;, CO, C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;, HCN, Ar, N&lt;sub&gt;2&lt;/sub&gt;, CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>85.97</td>
<td>86.40</td>
<td></td>
</tr>
<tr>
<td>Reduced Model 3</td>
<td>15</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O, O&lt;sub&gt;2&lt;/sub&gt;, O, OH, H&lt;sub&gt;2&lt;/sub&gt;, H, CO&lt;sub&gt;2&lt;/sub&gt;, CO, C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;, HCN, Ar, N&lt;sub&gt;2&lt;/sub&gt;, CH&lt;sub&gt;4&lt;/sub&gt;, CH&lt;sub&gt;3&lt;/sub&gt;, CH&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>88.06</td>
<td>86.59</td>
<td></td>
</tr>
<tr>
<td>Reduced Model 4</td>
<td>17</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O, O&lt;sub&gt;2&lt;/sub&gt;, O, OH, H&lt;sub&gt;2&lt;/sub&gt;, H, CO&lt;sub&gt;2&lt;/sub&gt;, CO, C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;, HCN, Ar, N&lt;sub&gt;2&lt;/sub&gt;, CH&lt;sub&gt;4&lt;/sub&gt;, CH&lt;sub&gt;3&lt;/sub&gt;, CH&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>88.07</td>
<td>87.07</td>
<td></td>
</tr>
<tr>
<td>Elementary Model</td>
<td>123</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O, O&lt;sub&gt;2&lt;/sub&gt;, O, OH, H&lt;sub&gt;2&lt;/sub&gt;, H, CO&lt;sub&gt;2&lt;/sub&gt;, CO, C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;, HCN, H&lt;sub&gt;2&lt;/sub&gt;S, Ar, N&lt;sub&gt;2&lt;/sub&gt;, CH&lt;sub&gt;4&lt;/sub&gt;, CH&lt;sub&gt;3&lt;/sub&gt;, CH&lt;sub&gt;2&lt;/sub&gt;O, C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;, C&lt;sub&gt;2&lt;/sub&gt;H4, C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;, C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;, C&lt;sub&gt;3&lt;/sub&gt;H, CH&lt;sub&gt;2&lt;/sub&gt;, CH, CH&lt;sub&gt;2&lt;/sub&gt;CO, HCO, HO&lt;sub&gt;2&lt;/sub&gt;, H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;, HNCO, HNO,CN,NCO, NNH, NH&lt;sub&gt;2&lt;/sub&gt;, NH, N&lt;sub&gt;2&lt;/sub&gt;O, NO, N</td>
<td>82.06</td>
<td>----</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.1:** The compositions of combustion product for six sets of kinetic reaction models.

### 3.1. ILLINOIS #6 COAL AIR FLAME

………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………...
CONCLUSIONS

Two devolatilization models, six reaction sets describing combustion of volatiles, and two char oxidation models were used to calculate species concentrations and particle temperatures for Illinois #6 and Pittsburgh #8 coal air flames. The combustion of coal char is described by the single-film model. The influence of radiative heat transfer between particles and a cold environment were also examined. The mass-mean particle sizes are 15.0 µm and 14.0 µm for Illinois #6 and Pittsburgh #8 coal, respectively.

Two devolatilization models called the multiple parallel reaction (MPRM) and distributed activation energy model (DAEM) were used for testing. There were 7 gases in the volatiles: CO₂, H₂O, CO, C₂H₆, CH₄, H₂ and HCN. There was no difference between the two models. For high temperatures, the devolatilization process occurs quickly and finishes about 3 - 5 mm (0.06 sec) from the burner.

Combustion (oxidation) of volatiles with and without char oxidation were also tested. There was five active gases, CO, C₂H₆, CH₄, H₂ and HCN in volatiles, three of which (CO, CH₄ and H₂) were most significant for coal combustion due to their high activities. Six different sets of kinetic reaction called global model, reduced model 1, 2, 3 and 4, and elementary model were used for testing. They varied from 3 reactions (global model) to 123 reactions (elementary model). All kinetic models described oxidations for CO, CH₄ and H₂, except the elementary model which described oxidations for all five active gases (CO, C₂H₆, CH₄, H₂ and HCN).

Without the char oxidation model, CO is the sole product of the pyrolysis process and it is quickly oxidized. All concentrations calculated without char oxidation model were too low compared with the experimental data. The particle temperatures were heated by hot gas by conduction and always lower than gas temperature.

With the char oxidation model, CO comes partly from the pyrolysis, partly from the char oxidation. Except for the elementary kinetic reaction model, all kinetic models were calculated with the char oxidation model. The elementary model with 123 reactions was too comprehensive to calculate with the char oxidation model (too many reactions). The concentrations for CO₂, O₂ and CO calculated with the reduced model 3 with 15 reactions agreed with the experimental data. This case is called the reference case. The amount of CH₄ was too small and therefore difficult to compare. The H₂ concentration was poor compared with experimental data. This is because is the H₂ may come from char oxidation (Eq.(95)) which has not been considered in the calculation. The particle temperatures obtained from this case agreed well with the experimental data. The largest difference between calculation and experiment was about 50.0 K. The error of particle temperature may come from the error of measurement of gas temperature. However, it is acceptable.

The burning of coal char is described by the single-film model. Both CO and CO₂ are the
heterogeneous products. Two different "reaction rates" called Mitchell's model (Model 1) and the model of Fields et al. (1967) (Model 2) were used. Although the results obtained with the char oxidation model 2 were in good agreement with the experimental data, the reaction rate of model 2 seems to be low and therefore the reaction between oxygen from the gas phase and fixed carbon of coal char was slower compared with the experimental data. Mitchell's model, where the apparent reaction order differed from unity, is complicated for calculation. The reaction between fixed carbon and oxygen from the surroundings was also slow compared with that of the experimental data. The model of Field et al. (1967) is suitable for calculating a coal air flame if the computational time is considered.

The composition of volatiles (mass fractions of single pyrolysis species), e.g. $Y_{\text{CO}_2}$, $Y_{\text{H}_2\text{O}}$, $Y_{\text{CO}}$, $Y_{\text{HCN}}$, $Y_{\text{C}_2\text{H}_6}$, $Y_{\text{CH}_4}$, $Y_{\text{H}_2}$ and $Y_{\text{S}}$ ($Y_{\text{H}_2\text{S}}$), are usually unknown and must be estimated. The values are calculated from the measured composition of volatiles of Solomon et al. (1992) (Table A4, APP.A1) and they are adjusted by multiplying with a Q-factor of 1.385 and 1.50 for Illinois #6 and Pittsburgh #8 coals, respectively. The ultimate analysis gives very sensitive results.

The pyrolysis process takes place very quickly, and there is therefore only a slight difference between results based on the assumptions that the char oxidation occur after and simultaneously with the pyrolysis process. But for small particles, the amount of gases released from coal by pyrolysis may be too small to prevent the oxygen from the gas phase being transported to the particle surface and reacting with it. Therefore, the assumption that the char oxidation process and the pyrolysis process occur at the same time is more corrected.

A knowledge of particle size is very important for calculation. The ignition of the small particles begins earlier and they are burnt faster than the large particles. The temperatures of large particles may be higher than the temperatures of small particles. The concentration profiles for three different particle sizes were also different because of different particle temperatures.

Three different oxygen concentrations in the oxidizer are were for testing. More CO$_2$ is produced with higher oxygen concentrations in the oxidizer. The CO$_2$ comes partly from the pyrolysis, partly from the char oxidation, and partly from the oxidation of CO in the gas phase. The CO concentration was also high but it was quickly oxidized in the gas phase. The CO concentration is high with a low oxygen concentration in the oxidizer. The heat generation by char oxidation depends on the oxygen concentration in the oxidizer because experiments were performed with fuel-rich mixture (equivalence ratio $\Phi = 2.14$ for Illinois #6 coal and $\Phi = 2.09$ for Pittsburgh #8 coal). The greater the oxygen concentration in the oxidizer, the greater the char oxidation and the more energy generated.

Both the radiation of particles to a cold environment and the radiation between particles influence the results. However, the influence of these radiations is small due to small amounts of particles. This influence may be more important with large amounts of particles.
The peak of particle temperature profiles is influenced most because the particle temperatures at this point are highest. The concentration profiles for the cases without radiation of particles to a cold environment and radiation between particles were slightly different compared with the reference case, due to different particle temperatures.

The results obtained for Illinois #6 coal were closer to the experimental data than those obtained for Pittsburgh #8 coal, because the amount of high hydrocarbon (e.g. C2H6) and (or) tar for Pittsburgh #8 coal was higher than for Illinois #6 coal. The soot formation in Pittsburgh #8 coal air flame may therefore be higher than that in Illinois #6 coal air flame.
REFERENCES


oxygen and total pressure on the surface oxidation rate of bituminous coal.  

Industrie (Paris), 91, pp. 269-275.

79-.

and Chemical Kinetic rate Limitations During Coal Rapid Pyrolysis. 20th  

Comprehensive Chemical Kinetic Mechanism for the Oxidation of Acetylene:  
Comparison of Model Predictions with Results from Flame and Shock Tube  
181-196.

34, pp. 149-176.

[56] Miller, J.A., Branch, M.C., Mclean, W.J., Chandler, D.W., Smooke, M.D., and  
Kee,R.J. (1984). The Conversion of HCN to NO and N₂ in H₂-O₂-HCN-Ar  
Flames at low pressure. 20th Symp. (Int.) on Combust., The Combust. Inst.,  
PA, pp. 673-684.

Burning Rates of Pulverized-Coal Char in Specified O₂ and CO₂ Environments.  

Reaction at The Surfaces of Burning Coal Char Particles. 22nd Symp. (Int.)  

CO Conversion in The Boundary Layers Surrounding Pulverized-Coal Char  
Particles. 23rd Symp. (Int.) on Combust., The Combust. Inst., pp. 1169- 
1176.

and cokes. Fuel, 61, pp. 713-716.

for Methane, Methanol and Propane Flames. 21st Symp. (Int.) on Combust.,  
The Combust. Inst., PA, pp.739-748.

on Devolatilization Yields from a Bituminous Coal. Ind. Eng. Chem. Res., 26,  
pp. 2378-2384.

Prepared for Lab. of Heating and Air Conditioning, Technical University of  
Denmark. Prepared by Dep. of Mechanical and Aerospace Engineering,  
Arizona State University, USA.


APPENDIX A1. Calculation of Composition of Volatiles from Raw Coal

Knowledge of the mass fractions of single pyrolysis species (composition of volatiles or volatile components), e.g. $Y_{CO_2}$, $Y_{H_2O}$, $Y_{CO}$, $Y_{HCN}$, $Y_{C_2H_6}$, $Y_{CH_4}$, $Y_{H_2}$ and $Y_{S}$ ($Y_S$), is very important. These mass fractions are usually unknown and must be calculated. The mass fractions for eight single pyrolysis species ($Y_{CO_2}$, $Y_{H_2O}$, $Y_{CO}$, $Y_{HCN}$, $Y_{C_2H_6}$, $Y_{CH_4}$, $Y_{H_2}$ and $Y_{S}$ ($Y_{H_2S}$)) can be calculated in the following way:

Coal is analysed in two ways: Ultimate and Proximate analysis.

### Ultimate analysis

<table>
<thead>
<tr>
<th>Component</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{C}$</td>
<td>$C$</td>
</tr>
<tr>
<td>$V_{H}$</td>
<td>$H$</td>
</tr>
<tr>
<td>$V_{O}$</td>
<td>$O$</td>
</tr>
<tr>
<td>$V_{N}$</td>
<td>$N$</td>
</tr>
<tr>
<td>$V_{S}$</td>
<td>$S$</td>
</tr>
<tr>
<td>$V_{H_2O}$</td>
<td>$H_2O$</td>
</tr>
<tr>
<td>$V_{Ash}$</td>
<td>$Ash$</td>
</tr>
</tbody>
</table>

### Proximate analysis

- $VM$ (Volatile matter)
- $FC$ (Fixed carbon)
- $V_{H_2O}$
- $V_{Ash}$

$\sum V_i = 1.00$

According to Solomon et al. (1992), there is no kinetic rate coefficient for sulfur and it equals the analysis value (the evolution of sulfur is not considered here).

$$A: \quad V_s^* = V_s^* \tag{A1}$$

$$B: \quad \sum V_{Nj} = \frac{14}{27} V_i^* - V_i^* = \frac{27}{14} V_{Nj} = \frac{27}{14} V_N \tag{A2}$$

$$C: \quad V_2^* = V_{H_2O}^* \tag{A3}$$

$$D: \quad \sum V_{Hi} = \frac{1}{27} V_4^* + \frac{6}{30} V_5^* + \frac{4}{16} V_6^* + V_7^* = V_H^* \tag{A4}$$

$$\sum_{=6} V_6^* = \frac{V_{H_2}^* - \frac{1}{27} V_4^*}{\frac{6}{30} Y_5^* + \frac{4}{16} Y_6^*} \tag{A5}$$
\[ E : \sum V_{ci} = \frac{12}{44} V_{i}^* + \frac{12}{28} V_{3}^* + \frac{12}{27} V_{4}^* + \frac{24}{30} V_{5}^* \]
\[ + \frac{12}{16} V_{6}^* + V_{7}^* = V_{c}^* \]  
(A6)

\[ \implies \frac{12}{44} V_{i}^* + \frac{12}{28} V_{3}^* = V_{c}^* \left\{ \frac{12}{27} V_{4}^* + \frac{24}{30} V_{5}^* + \frac{12}{16} V_{6}^* + V_{7}^* \right\} \]  
(A7)

\[ F : \sum V_{oji} = \frac{32}{34} V_{i}^* + \frac{16}{28} V_{3}^* = V_{o}^* \]  
(A8)

\[ \implies \frac{32}{34} V_{i}^* - \frac{16}{28} V_{3}^* = V_{o}^* \]  
(A9)

\[ V_{i}^* \quad Y_{1i}^* \quad \text{and} \quad V_{3}^* \quad Y_{3i}^* \quad \implies \quad V_{3}^* = (V_{1i}^* Y_{3i}^*)/Y_{1i}^* \]

Inserting \( V_{3}^* \) in Eq.(A9), gives

\[ V_{i}^* = \frac{34}{32} \left\{ V_{o}^* - \frac{16}{28} V_{3}^* \right\} \]  
(A10)

\[ \implies \left\{ \frac{32}{34} V_{i}^* + \frac{16}{28} V_{3}^* \right\} V_{i}^* = V_{o}^* \]  
(A11)

and

\[ V_{3}^* = \frac{28}{16} \left\{ V_{o}^* - \frac{32}{34} V_{i}^* \right\} \]  
(A12)

\( V_{i}^* \) should be equal to VM (volatile matter). Corrected values of mass fraction of species can be calculated as

\[ V_{i,corr}^{CO2} = V_{i,corr}^{CO2} = \frac{V_{i}^* VM}{\sum V_{i}^*} \]  
(A13)

\[ V_{3,corr}^{CO} = V_{3,corr}^{CO} = \frac{V_{3}^* VM}{\sum V_{i}^*} \]  
(A15)

\[ V_{4,corr}^{HCN} = V_{4,corr}^{HCN} = \frac{V_{4}^* VM}{\sum V_{i}^*} \]  
(A16)
where
\[
\sum_{i=1}^{n} V_i^* = \sum_{i=1}^{n} V_i^{* corr} - V_{H2O}^{* corr}
\]  

(A22)

The mass fractions of volatiles used in the calculations are shown in Table A1. They are calculated from the adjusted values of Illinois #6 and Pittsburgh #8 coal (Table A2).

Table A3 shows the analysis of raw coal. The values in column (2) are the adjusted values. In proximate analysis, the mass fractions of volatile matter, moisture and ash have the same values as the analysis values (column (1)); the mass fraction of fixed carbon is adjusted so that the total mass fraction is unity. In the ultimate analysis, the mass fractions of ash and moisture have the same values as the analysis values (column (1)); the other mass fractions, C, H, O, N, S, are adjusted so that the total mass fraction is also unity. In column (3) (only Illinois #6 coal) of the ultimate analysis table, the mass fractions of fixed carbon, ash and moisture are retained; the other mass fractions are adjusted.

Table A4 shows the composition of volatiles (mass fraction of single species in volatile matter). These values are used to calculate composition of volatiles from unknown coal.
Table A5 shows the proximate and ultimate analysis of raw coal.

<table>
<thead>
<tr>
<th></th>
<th>Illinois #6</th>
<th>Pittsburgh #8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
<td>(b)</td>
</tr>
<tr>
<td>(V^{*}_{CO_2,corr})</td>
<td>0.085</td>
<td>0.073</td>
</tr>
<tr>
<td>(V^{*}_{H_2O,corr})</td>
<td>0.066</td>
<td>0.073</td>
</tr>
<tr>
<td>(V^{*}_{CO,corr})</td>
<td>0.142</td>
<td>0.122</td>
</tr>
<tr>
<td>(V^{*}_{HCN,corr})</td>
<td>0.024</td>
<td>0.028</td>
</tr>
<tr>
<td>(V^{*}_{C_2H_6,corr})</td>
<td>0.082</td>
<td>0.090</td>
</tr>
<tr>
<td>(V^{*}_{CH_4,corr})</td>
<td>0.045</td>
<td>0.049</td>
</tr>
<tr>
<td>(V^{*}_{H_2,corr})</td>
<td>0.016</td>
<td>0.018</td>
</tr>
<tr>
<td>(V^{*}_S,corr)</td>
<td>0.046</td>
<td>0.053</td>
</tr>
<tr>
<td>Total</td>
<td>0.506</td>
<td>0.506</td>
</tr>
<tr>
<td>(V^{*}_{H_2O,corr})</td>
<td>0.059</td>
<td>0.059</td>
</tr>
<tr>
<td>(V^{*}_{vol})</td>
<td>0.447</td>
<td>0.447</td>
</tr>
<tr>
<td>Total</td>
<td>0.506</td>
<td>0.506</td>
</tr>
</tbody>
</table>

**Table A1:** The adjusted mass fractions of volatiles. \(V^{*}_{vol}\) is the adjusted volatile matter, equal to the analysis value times with the Q-factor (Q = 1.385 for Illinois #6 coal and Q = 1.50 for Pittsburgh #8 coal (Jensen and Mitchell (1993))). (a): The values used in Figs. D011, D012, D021 and D022. (b): The values used in the other calculations of Illinois #6 coal air flame. (c): The values used in all calculations of Pittsburgh #8 coal air flame.

<table>
<thead>
<tr>
<th></th>
<th>Illinois #6</th>
<th>Pittsburgh #8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
<td>(b)</td>
</tr>
<tr>
<td>(V^{<em>}_{a,act} = V^{</em>}<em>{CO} + V^{*}</em>{HCN} + V^{<em>}_{C_2H_6} + V^{</em>}<em>{CH_4} + V^{*}</em>{H_2})</td>
<td>0.309</td>
<td>0.307</td>
</tr>
<tr>
<td>(V^{<em>}_{b,act} = V^{</em>}<em>{CO} + V^{*}</em>{CH_4} + V^{*}_{H_2})</td>
<td>0.203</td>
<td>0.189</td>
</tr>
<tr>
<td>(V^{<em>}_{b,act}/V^{</em>}_{a,act})</td>
<td>0.657</td>
<td>0.616</td>
</tr>
<tr>
<td>(V^{<em>}_{a,act}/V^{</em>}_{vol})</td>
<td>0.691</td>
<td>0.687</td>
</tr>
<tr>
<td>(V^{<em>}_{C_2H_6}/V^{</em>}_{a,act})</td>
<td>0.265</td>
<td>0.293</td>
</tr>
<tr>
<td>(V^{<em>}_{C_2H_6}/V^{</em>}_{vol})</td>
<td>0.183</td>
<td>0.201</td>
</tr>
</tbody>
</table>

**Table A2:** Ratio of mass fractions of active gases and \(C_2H_6\) to mass fraction of total volatiles.
### Proximate Analysis

<table>
<thead>
<tr>
<th>Proximate Analysis</th>
<th>Blair Athol</th>
<th>Cerrejon</th>
<th>Illinois #6</th>
<th>Middleburgh</th>
<th>Pittsburgh #8</th>
<th>Ulan</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1) (2)</td>
<td>(1) (2)</td>
<td>(1) (2)</td>
<td>(1) (2)</td>
<td>(1) (2)</td>
<td>(1) (2)</td>
</tr>
<tr>
<td>% Volatile Matter (VM)</td>
<td>28.5 28.5</td>
<td>34.5 34.5</td>
<td>32.1 32.1</td>
<td>32.1 32.1</td>
<td>22.2 22.2</td>
<td>31.5 31.5</td>
</tr>
<tr>
<td>% Fixed Carbon (FC)</td>
<td>51.2 51.3</td>
<td>52.0 52.1</td>
<td>46.2 46.2</td>
<td>46.2 46.2</td>
<td>61.2 61.3</td>
<td>51.9 52.0</td>
</tr>
<tr>
<td>% Moisture</td>
<td>2.7 2.7</td>
<td>3.9 3.9</td>
<td>5.9 5.9</td>
<td>5.9 5.9</td>
<td>3.0 3.0</td>
<td>2.5 2.5</td>
</tr>
<tr>
<td>% Ash</td>
<td>17.5 17.5</td>
<td>9.5 9.5</td>
<td>15.8 15.8</td>
<td>15.8 15.8</td>
<td>13.5 13.5</td>
<td>14.0 14.0</td>
</tr>
<tr>
<td>Total</td>
<td>99.9 100.0</td>
<td>99.9 100.0</td>
<td>100.0 100.0</td>
<td>100.0 100.0</td>
<td>99.9 100.0</td>
<td>99.9 100.0</td>
</tr>
</tbody>
</table>

### Ultimate Analysis

<table>
<thead>
<tr>
<th>Ultimate Analysis</th>
<th>Blair Athol</th>
<th>Cerrejon</th>
<th>Illinois #6</th>
<th>Middleburgh</th>
<th>Pittsburgh #8</th>
<th>Ulan</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1) (2)</td>
<td>(1) (2)</td>
<td>(1) (2)</td>
<td>(1) (2)</td>
<td>(1) (2)</td>
<td>(1) (2)</td>
</tr>
<tr>
<td>% Carbon</td>
<td>65.2 64.81</td>
<td>68.1 66.99</td>
<td>57.5 54.61</td>
<td>57.5 54.61</td>
<td>68.9 68.6</td>
<td>67.2 67.13</td>
</tr>
<tr>
<td>% Hydrogen</td>
<td>4.2 4.18</td>
<td>4.87 4.79</td>
<td>4.21 4.00</td>
<td>4.00 4.00</td>
<td>3.77 3.75</td>
<td>4.66 4.65</td>
</tr>
<tr>
<td>% Nitrogen</td>
<td>1.62 1.61</td>
<td>1.47 1.45</td>
<td>1.20 1.14</td>
<td>1.20 1.14</td>
<td>1.72 1.71</td>
<td>1.39 1.39</td>
</tr>
<tr>
<td>% Sulfur</td>
<td>0.53 0.53</td>
<td>0.69 0.68</td>
<td>4.33 4.11</td>
<td>4.33 4.11</td>
<td>0.36 0.36</td>
<td>1.29 1.29</td>
</tr>
<tr>
<td>% Moisture</td>
<td>2.7 2.7</td>
<td>3.9 3.9</td>
<td>5.9 5.9</td>
<td>5.9 5.9</td>
<td>3.0 3.0</td>
<td>2.5 2.5</td>
</tr>
<tr>
<td>% Ash</td>
<td>17.5 17.5</td>
<td>9.5 9.5</td>
<td>15.8 15.8</td>
<td>15.8 15.8</td>
<td>13.5 13.5</td>
<td>14.0 14.0</td>
</tr>
<tr>
<td>Total</td>
<td>100.47 100.0</td>
<td>101.43 100.0</td>
<td>104.1 100.0</td>
<td>100.0 100.0</td>
<td>100.3 100.0</td>
<td>100.0 100.0</td>
</tr>
</tbody>
</table>
**Table A3:** Analysis of raw coal. *(1)*: as received; *(2),(3)*: corrected values
<table>
<thead>
<tr>
<th>Mass fraction</th>
<th>Zap North Dakota lignite</th>
<th>Gillette sub-bituminous</th>
<th>Montana Rosebud sub-bituminous</th>
<th>Illinois #6 bituminous</th>
<th>Pittsburgh #8 bituminous</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_1^*$ = $Y_{CO2}$</td>
<td>0.100</td>
<td>0.099</td>
<td>0.100</td>
<td>0.074</td>
<td>0.011</td>
</tr>
<tr>
<td>$Y_2^*$ = $Y_{H2O}$</td>
<td>(0.099)$^*$ 0.094</td>
<td>(0.067)$^*$ 0.062</td>
<td>0.102</td>
<td>(0.048)$^*$ 0.044</td>
<td>(0.028)$^*$ 0.022</td>
</tr>
<tr>
<td>$Y_3^*$ = $Y_{CO}$</td>
<td>0.194</td>
<td>0.154</td>
<td>0.068</td>
<td>0.123</td>
<td>0.092</td>
</tr>
<tr>
<td>$Y_4^*$ = $Y_{HCN}$</td>
<td>0.018</td>
<td>0.022</td>
<td>0.020</td>
<td>0.026</td>
<td>0.031</td>
</tr>
<tr>
<td>$Y_5^*$ = $Y_{C2H6}$</td>
<td>0.095</td>
<td>0.158</td>
<td>0.127</td>
<td>0.081</td>
<td>0.190</td>
</tr>
<tr>
<td>$Y_6^*$ = $Y_{CH4}$</td>
<td>0.025</td>
<td>0.043</td>
<td>0.034</td>
<td>0.044</td>
<td>0.050</td>
</tr>
<tr>
<td>$Y_7^*$ = $Y_{H2}$</td>
<td>0.017</td>
<td>0.012</td>
<td>0.013</td>
<td>0.016</td>
<td>0.012</td>
</tr>
<tr>
<td>$Y_8^*$ = $Y_{S}$ (organic) or $Y_{H2S}$</td>
<td>0.011</td>
<td>0.440</td>
<td>0.012</td>
<td>0.038</td>
<td>0.024</td>
</tr>
<tr>
<td>$Y_9^*$ = $Y_{NH3}$</td>
<td>0.001</td>
<td>0.000</td>
<td>0.001</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>C (nonvolatile)</td>
<td>0.440</td>
<td>0.440</td>
<td>0.520</td>
<td>0.550</td>
<td>0.562</td>
</tr>
<tr>
<td>$\Sigma Y_i^*$</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
</tbody>
</table>

**Table A4:** The composition of volatiles (Solomon et al. (1992)). *: The values in the parentheses are the "adjusted" values.
<table>
<thead>
<tr>
<th>Proximate Analysis</th>
<th>Blair Athol</th>
<th>Cerrejon</th>
<th>Illinois #6</th>
<th>Middleburgh</th>
<th>Pittsburgh #8</th>
<th>Ulan</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1)</td>
<td>(2)</td>
<td>(1)</td>
<td>(2)</td>
<td>(1)</td>
<td>(2)</td>
</tr>
<tr>
<td>% Volatile Matter (VM)</td>
<td>28.5</td>
<td>28.5</td>
<td>34.5</td>
<td>34.5</td>
<td>32.1</td>
<td>32.1</td>
</tr>
<tr>
<td>% Fixed Carbon (FC)</td>
<td>51.2</td>
<td>51.3</td>
<td>52.0</td>
<td>52.1</td>
<td>46.2</td>
<td>46.2</td>
</tr>
<tr>
<td>% Moisture</td>
<td>2.7</td>
<td>2.7</td>
<td>3.9</td>
<td>3.9</td>
<td>5.9</td>
<td>5.9</td>
</tr>
<tr>
<td>% Ash</td>
<td>17.5</td>
<td>17.5</td>
<td>9.5</td>
<td>9.5</td>
<td>15.8</td>
<td>15.8</td>
</tr>
<tr>
<td>Total</td>
<td>99.9</td>
<td>100.0</td>
<td>99.9</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ultimate Analysis</th>
<th>Blair Athol</th>
<th>Cerrejon</th>
<th>Illinois #6</th>
<th>Middleburgh</th>
<th>Pittsburgh #8</th>
<th>Ulan</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1)</td>
<td>(2)</td>
<td>(1)</td>
<td>(2)</td>
<td>(1)</td>
<td>(2)</td>
</tr>
<tr>
<td>% Carbon</td>
<td>65.2</td>
<td>64.81</td>
<td>68.1</td>
<td>66.99</td>
<td>57.5</td>
<td>54.61</td>
</tr>
<tr>
<td>% Hydrogen</td>
<td>4.2</td>
<td>4.18</td>
<td>4.87</td>
<td>4.79</td>
<td>4.21</td>
<td>4.00</td>
</tr>
<tr>
<td>% Nitrogen</td>
<td>1.62</td>
<td>1.61</td>
<td>1.47</td>
<td>1.45</td>
<td>1.20</td>
<td>1.14</td>
</tr>
<tr>
<td>% Sulfur</td>
<td>0.53</td>
<td>0.53</td>
<td>0.69</td>
<td>0.68</td>
<td>4.33</td>
<td>4.11</td>
</tr>
<tr>
<td>% Moisture</td>
<td>2.7</td>
<td>2.7</td>
<td>3.9</td>
<td>3.9</td>
<td>5.9</td>
<td>5.9</td>
</tr>
<tr>
<td>% Ash</td>
<td>17.5</td>
<td>17.5</td>
<td>9.5</td>
<td>9.5</td>
<td>15.8</td>
<td>15.8</td>
</tr>
<tr>
<td>Total</td>
<td>100.47</td>
<td>100.0</td>
<td>101.43</td>
<td>100.0</td>
<td>104.14</td>
<td>100.0</td>
</tr>
</tbody>
</table>
Table A5: Analysis of raw coal. (1): as received; (2),(3): corrected values.
APPENDIX A2. Numerical Calculation of DAEM for the Non-isothermal Process

\[
\frac{V_i^*-V_{ij}}{V_i^*} = \int_0^{E_{\text{max}}} \exp\left(\int_0^{t_j} k_{ij} \, dt\right) f_i(E) \, dE = \int_0^{E_{\text{min}}} \exp\left(\int_0^{t_j} k_{ij} \, dt\right) f_i(E) \, dE \quad (A23)
\]

where

\[
f_i(E) = \frac{1}{\sigma_i (2\pi)^{3/2}} \exp\left(\frac{- (E_i - E_0)}{2 \sigma_i^2}\right) \quad (A24)
\]

\[
k_i = k_{ij} \exp\left(-\frac{E_i}{RT}\right) \quad (A25)
\]

For

\[
j = 1: \quad \frac{V_i^*-V_{ij}}{V_i^*} = \int_{E_{\text{min}}}^{E_{\text{max}}} \exp\left(\int_0^{t_j} k_{ij} \, dt\right) f_i(E) \, dE \quad (A26)
\]

\[
j = 2: \quad \frac{V_i^*-V_{ij}}{V_i^*} = \int_{E_{\text{min}}}^{E_{\text{max}}} \left[ \int_{t_2}^{t_1} k_{ij} \, dt + \int_{t_2}^{t_1} k_{ij} \, dt \right] f_i(E) \, dE \quad (A27)
\]

\[
j = 3: \quad \frac{V_i^*-V_{ij}}{V_i^*} = \int_{E_{\text{min}}}^{E_{\text{max}}} \left[ \int_{t_3}^{t_2} k_{ij} \, dt + \int_{t_3}^{t_2} k_{ij} \, dt + \int_{t_3}^{t_2} k_{ij} \, dt \right] f_i(E) \, dE \quad (A28)
\]

or

\[
\frac{V_i^*-V_{ij}}{V_i^*} = \int_{E_{\text{min}}}^{E_{\text{max}}} \exp\left(- \int_{t_2}^{t_1} k_{ij} \Delta t_i + k_{ij} \Delta t_2 + \cdots + k_{ij} \Delta t_j \right) f_i(E) \, dE \quad (A29)
\]

where \(\Delta t_j = t_{j+1} - t_j\)