MATHEMATICAL MODELING
OF CARBON BLACK PROCESS FROM COAL

A Thesis Presented to
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THIS THESIS ENTITLED
"MATHEMATICAL MODELING
OF CARBON BLACK PROCESS FROM COAL"

by Qingjun Ji

has been approved
for the Department of Chemical Engineering
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1.1 SIGNIFICANCE OF RESEARCH

Carbon black can be ranked as one of the oldest manufactured products. Its usage as a pigment for the production of inks and mural paints can be traced back to the ancient Chinese and Egyptians. However, it was after the invention of movable type in the fifteenth century, the demand for carbon black pigment increased steadily.

The most important event, which had greatest influence on the usage of carbon black, occurred at the turn of the century. It involved the discovery of the reinforcing effect of carbon blacks when added to natural rubber. By using carbon black as reinforcing filler, the service life of a tire was increased tens of thousand kilometers. Today carbon black plays an important role, not only as a reinforcing filler for tires and other rubber goods but also as a pigment for printing inks, coatings, plastics, and a variety of other applications.

However, the carbon black industry itself has confronted the problem of procuring satisfactory feedstock in sufficient supply. In the early days of the industry, channel blacks produced from natural gas comprised the bulk of the carbon black market. As new uses for natural gas were uncovered, the price of natural gas was gradually increased. The main feedstock was changed to oil and coal tar. After the energy crisis of 1971, oils became more expensive. Consequently, coal may well be the future feedstock for the carbon black industry.
A number of processes have been patented to produce carbon black from coal (Johnson, 1966; Iyengar, 1971; Cheng, 1976, 1980, 1981; Chen & Savage, 1986). These processes have not yet been commercialized. The increasing cost of oil might accelerate industrial development of these processes.

Modeling is an important tool to guide process development. The goal of this study is to develop a computational model with a well-understood range of validity. This model can then be used in a predictive role to evaluate the feasibility and validity of new ideas. It can also be used to interpret experimental measurements, to extend our knowledge to new parameter regimes, and perhaps to design the process.

In a typical industrial operation, energy required for pyrolysis or partial combustion of the raw material is supplied by the complete combustion of a fuel. The mixing between combustion products and raw materials in minimized best can not be eliminated. A good model should also qualify this mixing.

There are many modeling works for carbon black industry, with gases (mainly methane) or liquid (benzene, petrochemical oils) as initial feedstock. But there is no modeling work for carbon black generated from solid feedstock (mainly, coal) at the point when this research was done.

1.2 OBJECTIVE OF RESEARCH

This research aims to develop a computer code for carbon black process, particularly for carbon blacks generated from coal.
The proposed model is based on previous modeling work: carbon black from methane and carbon black from benzene. These models will be reviewed and modified in this work. Therefore our computer code can be applied to carbon black process from natural gas, oil, as well as coal.

Like the previous models, constant temperature and plug flow are assumed. At this time, it does not predict the reactor temperature, temperature profile and radial variation of carbon black.

The most important physical properties of carbon black are particle, surface area and structure. All the distinct grades of carbon blacks can be identified by these three properties. This work will emphasize on modeling to predict the particle size and size distribution.
2.1 REVIEW OF CARBON BLACK PROCESS

2.1.1 FEEDSTOCK OF CARBON BLACK

Hydrocarbons, such as natural gas, acetylene, aromatics oils, are the raw materials on which the production of all carbon blacks is based (Kahre, 1964; Roger and Brown, 1962; Robertson, 1968; Kulik, 1961; Parker, 1962). According to the shape of the carbon black particles it can be concluded that they are formed in the gas phase. Carbon black particles and aggregates resemble those of other products obtained by pyrogenic processes, such as those found in fumed silica (Donnet, 1993). One major prerequisite, therefore, is that the carbon black feedstock must be capable of being completely converted into the gaseous state. Consequently, the feedstock used are either gases or liquids which can be vaporized under the given reaction conditions.

On account of its availability, natural gas is the most frequently used raw material among the gaseous hydrocarbons. The preferred raw materials for other production processes of carbon black, besides natural gas, are oils that have a high content of aromatic hydrocarbons. Aromatics containing a number of condensed rings are particularly advantageous in terms of production yield, since the C/H ratio increases with the number of rings. The absence of side chains also improves the C/H ratio, and aromatics without side chains are therefore preferred. In practice, both carbonchemical and petrochemical oils are used as feedstock sources (TABLE 2.1).
TABLE 2.1 Process feedstock yielding carbon black (Donnet, 1993)

<table>
<thead>
<tr>
<th>Type of feedstock</th>
<th>Raw material/Source</th>
<th>Manufacturing process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonchemical Oils</td>
<td></td>
<td>Distillation to obtain washing oils, electrode pitch and other carbonaceous materials.</td>
</tr>
<tr>
<td>Coal tar oils</td>
<td>Unrefined coal tar</td>
<td>Distillation to obtain washing oils, electrode pitch and other carbonaceous materials.</td>
</tr>
<tr>
<td>Petrochemical Oils</td>
<td></td>
<td>Steam cracking to produce ethylene, propylene, and other olefins.</td>
</tr>
<tr>
<td>Steam cracker oils</td>
<td>Naphtha, gas oil</td>
<td>Steam cracking to produce ethylene, propylene, and other olefins.</td>
</tr>
<tr>
<td>Catcracking oils</td>
<td>Heavy petroleum fraction</td>
<td>Fluid catcracking processes to produce gasoline.</td>
</tr>
<tr>
<td>Aromatic concentrates</td>
<td>Distillation residues from oil refineries</td>
<td>Extraction with furfural to obtain greases and lubricating oils.</td>
</tr>
</tbody>
</table>

2.1.2 PROCESSES TO PRODUCE CARBON BLACK

From a chemical point of view, it is essential to classify carbon black manufacturing processes into two categories of incomplete combustion and thermal decomposition of hydrocarbons, depending upon the presence or absence of oxygen. In terms of quantity, the incomplete combustion process is by far the most important one (furnace black). The second process, the thermal decomposition of hydrocarbons (thermal black) in the absence of oxygen, plays only a very limited role.

The raw materials consist of gaseous or liquid hydrocarbons. For a better understanding of the process, they are differentiated into fuel and feedstock, although the limits between these materials are not clearly defined. Natural gas is the most frequently used fuel due to its ease of handling, whereas the feedstocks are comprised of the various types of oils described previously.

The ratio of the two materials depends on the carbon black's quality. Changes in
the ratio between the fuel and the feedstock affect carbon black properties such as size and size distribution.

In a typical furnace reactor, the first section of the reactor is the combustion zone, where the fuel is burned in an excess of process air. In the subsequent section, the mixing zone, the carbon black feedstock is added and mixed as homogeneously as possible with the hot gases from the combustion chamber. In the third section, the reaction zone, a minor portion of feedstock reacts with the remaining oxygen from the combustion chamber, but the major portion of the feedstock is pyrolyzed and decomposed into carbon black and off-gas. In the final section, the quench zone, the mixture resulting from the reaction is cooled by injection of water.

The full reaction zone could be roughly divided into two parts: the primary and secondary reaction zone. The pyrolysis of feedstock and carbon formation reaction take place in the primary reaction zone (about 1.2 to 2 msec); the growth and oxidation reactions take place in the secondary reaction zone (about 12 to 20 msec.) (Lewis, 1974).

2.1.3 MECHANISMS OF CARBON BLACK PROCESS

Several theories have been proposed for the formation of particulate carbon but no mechanism could explain the formation from all flames regardless of their nature or the type of fuel. However, it is now agreed that the formation of carbon black involves the following different stages (Jensen, 1972; Ivie and Ferney, 1985; Donnet, 1993):
Nucleation or formation of carbon black precursors and carbon black inception that involves the transformation of a molecular system to a particulate system.

Aggregation of particles that involves collisions between the large number of tiny particles with dimension in the order 1-2 nm produced by nucleation. This results in the formation of larger spherical particles with dimensions in the order 10-50 nm.

Aggregation or agglomeration of these spherical particles into chains approximately up to 1 mm in length.

The coagulation rate constants between particles can be calculated by following literature formula:


\[ \kappa_{ij} = (NkTv / 2)^{1/2} \left[ \left( r_i + r_j \right) / 4 \right] \left( r_i + r_j \right) r_i^3 r_j^3 \]  

(2.1)

where,

- \( \kappa_{ij} \) = coagulation rate constant for the particle \( i \) and \( j \);
- \( N \) = Avogadro number \( (6.023 \times 10^{23}) \);
- \( k \) = Boltzmann constant \( (1.3807 \times 10^{-16} \text{ Joule/K}) \);
- \( T \) = Temperature (K);
- \( v \) = specific (atomic carbon) condensed phase volume of \( 1 \times 10^{23} \);
- \( r_i \) = radius of particle \( i \), (nm);
(B). Proposed by Fuch (1989)

\[
\kappa_{\alpha ij} = 4\pi (D_i + D_j)(r_i + r_j) \left[ \frac{r_i + r_j}{r_i + r_j + g_j} + \frac{4(D_i + D_j)}{(C_i^2 + C_j^2)^{1/2} (r_i + r_j)} \right]^{-1} \tag{2.2}
\]

where

\begin{align*}
\kappa_{\alpha ij} & = \text{coagulation rate constant for the particle } i \text{ and } j; \\
D_i & = \text{diffusion coefficient of particle } i; \\
r_i & = \text{radius of particle } i; \\
C_i & = \text{mean thermal velocity of particle } i; \\
l_i & = \text{mean free path of particle } i \ (8D_i/\pi C_i); \\
g_i & = \frac{(1/6r_i)(2r_i+l_i)^3 - (4r_i^2+l_i^2)3^{1/2}}{2r_i}; \\
g_{ij} & = (g_i^2+g_j^2)^{1/2};
\end{align*}

(C). Proposed by Forney (1994)

\[
\kappa_{\alpha ij} = 2\pi (T)(Boltz)(r_i + r_j)(B_i + B_j)(\frac{1.0}{1.0 + F}) \tag{2.3}
\]

where

\begin{align*}
\kappa_{\alpha ij} & = \text{coagulation rate constant for the particle } i \text{ and } j; \\
T & = \text{temperature, K}; \\
\pi & = 3.14159; \\
Boltz & = \text{Boltzmann constant } 1.3807\times10^{-16}; \\
r_i & = \text{radius of particle } i; \\
B_i & = \frac{[1.0+0.864\times UD_i+0.29\times UD_i\times exp(-1.25/UD_i)]/(6.0\pi\times Vl\times r_i)}}{r_i};
\end{align*}
\[
F = 4.0 \times [(DIF_i + DIF_j)/(r_i + r_j)] \times [\pi w/(8.0 \times \text{Boltz} \times T)]^{0.5};
\]

To get \( B_i \) and \( F \):

\[
VIS = 1.81 \times 10^{-4} \times (1.0/293.0^{0.5}) \times (1.0 + 111.3/293.0) \times T^{1.5}/(T + 111.3);
\]

\( \text{Pres} \) = pressure of reactor, atm (assume \( \text{Pres} = 1 \));

\( \text{Con} = 12.0/6.023 \times 10^{23}; \)

\( Cnu_i \) = number of carbon atoms in particle class \( i \);

\( w = Cnu_i \times Cnu_j \times \text{Con}/(Cnu_i \times Cnu_j) \);

\( UD_i = (2.18 \times 10^{-8} \times T/\text{Pres})/r_i; \)

\( DIF_i = \text{Boltz} \times T \times B_i; \)

2.2 TWO MODELS FOR CARBON BLACK GENERATION

2.2.1 CARBON BLACK FROM METHANE

Experimental work on the formation of carbon black from gaseous hydrocarbons is plentiful but often apparently contradictory and difficult to assimilate. The mechanisms advocated include dehydrogenation and polymerization via acetylenes, polymerization via aromatics, condensation and graphitization, and so on, but none of these mechanisms have been put on a firm quantitative footing.
Jensen (1974) raised an approach to the prediction of carbon black formation from methane. In that approach, he considered five processes leading to the production of carbon black from gaseous hydrocarbons: gas reactions, nucleation, coagulation, growth, and oxidation. Because this process is so fuel-rich, we move oxidation to section 2.2.2.4 (OXIDATION). Nine pyrolysis reactions were considered to be the minimum set, which provides a reasonable description of the formation of C₂, C₂H, C₂H₂, and the intermediate species from CH₄. Carbon black particle size was divided into 15 discrete particle-classes according to the radius (Pₐ-P₀). The detailed information about each particle class is listed in Tables 2.2.

**TABLE 2.2 Particle class and growth rate constant (Jensen 1974)**

<table>
<thead>
<tr>
<th>Particles</th>
<th>Radius, (nm)</th>
<th>Carbon atoms per particle</th>
<th>κᵢ, ml/molecule*s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pₐ</td>
<td>0.2</td>
<td>4</td>
<td>1.4 × 10⁻¹⁰</td>
</tr>
<tr>
<td>P₉</td>
<td>0.38</td>
<td>23</td>
<td>6.0 × 10⁻¹⁰</td>
</tr>
<tr>
<td>P₉</td>
<td>0.95</td>
<td>360</td>
<td>3.2 × 10⁻⁹</td>
</tr>
<tr>
<td>P₉</td>
<td>2.3</td>
<td>5080</td>
<td>1.9 × 10⁸</td>
</tr>
<tr>
<td>P₉</td>
<td>5.7</td>
<td>7.8 × 10⁴</td>
<td>1.2 × 10⁻⁷</td>
</tr>
<tr>
<td>P₉</td>
<td>15</td>
<td>1.44 × 10⁶</td>
<td>8.2 × 10⁻⁷</td>
</tr>
<tr>
<td>P₉</td>
<td>32</td>
<td>1.32 × 10⁷</td>
<td>3.6 × 10⁻⁶</td>
</tr>
<tr>
<td>P₉</td>
<td>63</td>
<td>1.06 × 10⁸</td>
<td>1.4 × 10⁻⁵</td>
</tr>
<tr>
<td>P₉</td>
<td>150</td>
<td>1.47 × 10⁹</td>
<td>8.3 × 10⁻⁵</td>
</tr>
<tr>
<td>P₉</td>
<td>380</td>
<td>2.32 × 10¹⁰</td>
<td>5.2 × 10⁻⁴</td>
</tr>
<tr>
<td>P₉</td>
<td>790</td>
<td>2.07 × 10¹¹</td>
<td>2.2 × 10⁻³</td>
</tr>
<tr>
<td>P₉</td>
<td>1600</td>
<td>1.66 × 10¹²</td>
<td>9.0 × 10⁻³</td>
</tr>
<tr>
<td>P₉</td>
<td>3800</td>
<td>2.31 × 10¹³</td>
<td>5.2 × 10⁻²</td>
</tr>
<tr>
<td>P₉</td>
<td>7900</td>
<td>2.07 × 10¹⁴</td>
<td>5.2 × 10⁻¹</td>
</tr>
<tr>
<td>P₉</td>
<td>16000</td>
<td>1.66 × 10¹⁵</td>
<td>---</td>
</tr>
</tbody>
</table>
In this table, the radius column shows the physical size of each particle class. The carbon atom column shows how many carbon atoms need to form that specific particle class. The last column \( (\kappa_{1j}) \) lists the rate constants between each particle class and the growth species \( (G) \), which will be discussed in 2.2.1.2 (NUCLEATION) and 2.2.1.4 (GROWTH) sections.

2.2.1.1 GAS REACTIONS

\[
\begin{align*}
\text{CH}_4 & \rightleftharpoons \cdot\text{CH}_3 + \cdot\text{H} & (2.4) \\
\text{CH}_4 + \cdot\text{H} & \rightleftharpoons \cdot\text{CH}_3 + \text{H}_2 & (2.5) \\
\cdot\text{CH}_3 + \cdot\text{CH}_3 & \rightleftharpoons \text{C}_2\text{H}_6 & (2.6) \\
\text{C}_2\text{H}_6 + \cdot\text{H} & \rightleftharpoons \cdot\text{C}_2\text{H}_5 + \text{H}_2 & (2.7) \\
\cdot\text{C}_2\text{H}_5 & \rightleftharpoons \text{C}_2\text{H}_4 + \cdot\text{H} & (2.8) \\
\text{C}_2\text{H}_4 + \cdot\text{H} & \rightleftharpoons \cdot\text{C}_2\text{H}_3 + \text{H}_2 & (2.9) \\
\cdot\text{C}_2\text{H}_3 + \text{Ar} & \rightleftharpoons \text{C}_2\text{H}_2 + \cdot\text{H} + \text{Ar} & (2.10) \\
\text{C}_2\text{H}_2 + \cdot\text{H} & \rightleftharpoons \cdot\text{C}_2\text{H} + \text{H}_2 & (2.11) \\
\cdot\text{C}_2\text{H} + \cdot\text{H} & \rightleftharpoons \text{C}_2 + \text{H}_2 & (2.12)
\end{align*}
\]

All reactions (Eq.2.4 ~ Eq.2.12) above are reversible. The forward reaction rate constants are listed in TABLE 2.3 together with the equilibrium constants, from which backward reaction rate constants could be calculated. The units for the rate constants depended on the order of the chemical reaction. To calculate the rate, the concentration is expressed in term of number of molecules per cubic centimeter.
TABLE 2.3 Methane pyrolysis reaction constants (Jensen 1974)

<table>
<thead>
<tr>
<th>Rate Constant $a$</th>
<th>Equilibrium Constant</th>
<th>Reaction Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.7 \times 10^{-12}$</td>
<td>$1.7 \times 10^{-26} \exp(51300/T)$</td>
<td>(2.4)</td>
</tr>
<tr>
<td>$3.0 \times 10^{-10} \exp(-6000/T)$</td>
<td>$24 \exp(-30/T)$</td>
<td>(2.5)</td>
</tr>
<tr>
<td>$1.0 \times 10^{-10} \exp(-1400/T)$</td>
<td>$2.1 \times 10^{-27} \exp(43600/T)$</td>
<td>(2.6)</td>
</tr>
<tr>
<td>$2.0 \times 10^{-10} \exp(-5000/T)$</td>
<td>$9.4 \exp(1360/T)$</td>
<td>(2.7)</td>
</tr>
<tr>
<td>$2.8 \times 10^{-10} \exp(-20400/T)$</td>
<td>$9.3 \times 10^{23} \exp(-17000/T)$</td>
<td>(2.8)</td>
</tr>
<tr>
<td>$3.0 \times 10^{-10} \exp(-3460/T)$</td>
<td>$6.3 \exp(-590/T)$</td>
<td>(2.9)</td>
</tr>
<tr>
<td>$3.6 \times 10^{-10} \exp(-15600/T)$</td>
<td>$3.6 \times 10^{24} \exp(-20400/T)$</td>
<td>(2.10)</td>
</tr>
<tr>
<td>$3.0 \times 10^{-10} \exp(-9500/T)$</td>
<td>$4.5 \exp(-2600/T)$</td>
<td>(2.11)</td>
</tr>
<tr>
<td>$1.0 \times 10^{-10} \exp(-18000/T)$</td>
<td>$2.3 \exp(-16600/T)$</td>
<td>(2.12)</td>
</tr>
</tbody>
</table>

*a Unit: one molecule reaction, s$^{-1}$; two molecule reactions, ml molecule$^{-1}$s$^{-1}$; and so on.

2.2.1.2 NUCLEATION

It was assumed that nucleation created only the first class of particle, all the other particles are generated by coagulation between particles and growth of particles. The first class of particles, $P_A$, contained four carbon atoms. It was produced when a nucleus $N$ ($C_2$ or $C_2H$) collided with the growth species $G$ ($C_2$, $C_2H$ or $C_2H_2$). The hydrogen released, $v$, depended on the species involved in the reaction. The nucleation was described by chemical reaction (2.13). This reaction is considered non-reversible, and the rate coefficient was $1.0 \times 10^{-10}$ s$^{-1}$.

$$N + G \rightarrow P_A + (v/2) H_2$$ (2.13)
2.2.1.3 COAGULATION

Fifteen particle classes were considered as shown in TABLE 2.2. All particles except the largest were permitted to coagulate irreversibly with all others. The coagulation was also described by chemical reaction of the type:

\[ vP_i + P_j \rightarrow P_{j+1} \] (2.14)

where \( i, j \) run alphabetically from A to O, and \( i < j \). \( v \) is the number of class \( P_i \) particle determined from carbon balance.

The coagulation rate expressions were similar to that of a chemical reaction, and were dynamically calculated by using Eq.2.1.

2.2.1.4 GROWTH

Growth is the reaction in which one class of particle adds a certain amount of growth species, and becomes one class higher particle. Particle growth was calculated using equations similar to that for coagulation.

\[ P_i + G \rightarrow P_{i+1} + vH_2 \] (2.15)

The growth rate constants (\( \kappa_{1i} \)) were listed in TABLE 2.2. They are based on the assumption that each collision of the growth species \( G \) (C\(_2\), C\(_2\)H, C\(_2\)H\(_2\)) at a particle surface results in assimilation of the growth species into the particle.

The predicted results are reproduced in FIGURE 2.1 and FIGURE 2.2. All components are shown in FIGURE 2.1. The particle size distributions at different reaction times are shown in FIGURE 2.2.
Initial $[\text{CH}_4] = \text{6.0E19 molecules/ml}$,
Initial $[\text{H}_2] = \text{2.5E19 molecules/ml}$,
Initial $[\text{M}] = \text{2.6E20 molecules/ml}$, (M=Argon)
Temperature $= \text{1523K}$
2.2.2 CARBON BLACK FROM BENZENE

J.J. Ivie and L.J. Forney (1988) developed a numerical model of the synthesis of carbon black by benzene. This approach, patterned after Jensen (1974), assumes that four steps control particle formation: gas phase reactions, nucleation, growth and coagulation, and oxidation. The gas phase reactions are different compared to Jensen's reaction set. It is described by 15 reactions in which the phenyl radical is treated as the important intermediate in the formation of carbon black.
A discrete distribution of 10 particle radii is also used to approximate the simultaneous growth and coagulation of spherical carbon particles. The first two particles are different from Jensen's particle classification because of the difference in feedstock.

TABLE 2.4 Particle class proposed by Ivie and Forney (1988)

<table>
<thead>
<tr>
<th>Particle classes</th>
<th>Number of carbon atom</th>
<th>Particle diameter, (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_A )</td>
<td>14</td>
<td>0.64</td>
</tr>
<tr>
<td>( P_B )</td>
<td>50</td>
<td>0.98</td>
</tr>
<tr>
<td>( P_C )</td>
<td>360</td>
<td>1.90</td>
</tr>
<tr>
<td>( P_D )</td>
<td>5080</td>
<td>4.6</td>
</tr>
<tr>
<td>( P_E )</td>
<td>( 7.8 \times 10^4 )</td>
<td>11.0</td>
</tr>
<tr>
<td>( P_F )</td>
<td>( 1.44 \times 10^6 )</td>
<td>30.0</td>
</tr>
<tr>
<td>( P_G )</td>
<td>( 1.32 \times 10^7 )</td>
<td>64.0</td>
</tr>
<tr>
<td>( P_H )</td>
<td>( 1.06 \times 10^8 )</td>
<td>130.0</td>
</tr>
<tr>
<td>( P_I )</td>
<td>( 1.47 \times 10^9 )</td>
<td>300.0</td>
</tr>
<tr>
<td>( P_J )</td>
<td>( 2.32 \times 10^{10} )</td>
<td>760.0</td>
</tr>
</tbody>
</table>

2.2.2.1 GAS REACTIONS

The reaction set is listed from Equation (2.16) through (2.26). The reaction rate constants are listed in TABLE 2.5.

\[
\begin{align*}
\text{C}_6\text{H}_6 & \rightarrow \cdot\text{C}_6\text{H}_5 + \cdot\text{H} \\
\text{C}_6\text{H}_6 + \cdot\text{H} & \Leftrightarrow \cdot\text{C}_6\text{H}_5 + \text{H}_2 \\
\text{C}_6\text{H}_6 + \cdot\text{C}_6\text{H}_5 & \Leftrightarrow \text{C}_{12}\text{H}_{10} + \cdot\text{H}
\end{align*}
\]
TABLE 2.5 Benzene pyrolysis and oxidation constants proposed by Ivie and Forney (1988)

<table>
<thead>
<tr>
<th>Rate Constant</th>
<th>Reverse Rate Constant</th>
<th>Reaction Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5.0 \times 10^{15}\exp(452/RT)$</td>
<td>Not considered</td>
<td>(2.16)</td>
</tr>
<tr>
<td>$2.5 \times 10^{11}\exp(67/RT)$</td>
<td>$3.1 \times 10^{9}\exp(71/RT)$</td>
<td>(2.17)</td>
</tr>
<tr>
<td>$4.0 \times 10^{09}\exp(50/RT)$</td>
<td>$1.3 \times 10^{13}\exp(13/RT)$</td>
<td>(2.18)</td>
</tr>
<tr>
<td>$7.9 \times 10^{14}\exp(0/RT)$</td>
<td>$1.3 \times 10^{4}\exp(0/RT)$</td>
<td>(2.19)</td>
</tr>
<tr>
<td>$1.6 \times 10^{12}\exp(343/RT)$</td>
<td>Not considered</td>
<td>(2.20)</td>
</tr>
<tr>
<td>$6.3 \times 10^{10}\exp(251/RT)$</td>
<td>Not considered</td>
<td>(2.21)</td>
</tr>
<tr>
<td>$3.2 \times 10^{11}\exp(25/RT)$</td>
<td>Not considered</td>
<td>(2.22)</td>
</tr>
<tr>
<td>$2.1 \times 10^{10}\exp(19/RT)$</td>
<td>Not considered</td>
<td>(2.23)</td>
</tr>
<tr>
<td>$1.0 \times 10^{08}\exp(76/RT)$</td>
<td>Not considered</td>
<td>(2.24)</td>
</tr>
<tr>
<td>$2.2 \times 10^{11}\exp(70/RT)$</td>
<td>Not considered</td>
<td>(2.25)</td>
</tr>
<tr>
<td>$1.0 \times 10^{09}\exp(8/RT)$</td>
<td>Not considered</td>
<td>(2.26)</td>
</tr>
</tbody>
</table>

*Unit: one molecule reaction, s$^{-1}$; two molecule reactions, ml molecule$^{-1}$s$^{-1}$; and so on.
2.2.2.2 NUCLEATION

Because of different feedstock, the nucleation (Eq.2.13) is re-designed for benzene. \( \mathbf{P_A} \), which is a 14-carbon-atom particle now, produced when a nucleus \( \mathbf{N} \) (\( \text{C}_6\text{H}_5 \) or \( \text{C}_{12}\text{H}_{10} \)) collided with the growth species \( \mathbf{G} \) (\( \text{C}_2\text{H}_3 \), \( \text{C}_2\text{H}_2 \), or \( \text{C}_4\text{H}_3 \)). The hydrogen released, \( \nu \), depended on the species involved in the reaction. \( n \) is the number of \( \mathbf{G} \) determined from carbon balance

\[
\mathbf{N} + n \mathbf{G} \rightarrow \mathbf{P_A} + \left(\frac{\nu}{2}\right) \mathbf{H}_2 \tag{2.27}
\]

2.2.2.3 COAGULATION AND GROWTH

Same as the discussion in Eq.2.14 and Eq.2.15 except for the coagulation constant calculation formula. The formula Ivie and Forney used is shown in Eq.2.2.

2.2.2.4 OXIDATION

Particle oxidation was treated in a manner analogous to that used for the coagulation, which means that \( \text{OH} \) is considered as one of the particles. The coagulation rate constants (or rather, the reaction rate constants) between \( \text{OH} \) and the different particles can be calculated using the formula used in section (2.2.1.3 COAGULATION).

\[
\mathbf{P}_1 + \text{OH} \rightarrow \mathbf{P}_{1,A} + \text{CO} + \frac{1}{2} \mathbf{H}_2 \tag{2.28}
\]

Fenimore and Jones (1967) suggested that every tenth collision between an \( \text{OH} \) molecule and a particle results in the oxidation of a carbon atom. Therefore we took one tenth of the calculated coagulation constant as the oxidation rate constant.
Using the mechanism above, the predictions of the concentration profiles are reproduced in FIGURE 2.3 (Ivie and Forney, 1988). The conditions used in the numerical code for these results consisted of a temperature of 1,800 K and an equivalence ratio (stoichiometric oxygen for complete combustion of benzene divided by available oxygen) of $\phi = 5.5$.

One of main problems of this model is that CO$_2$ and H$_2$O are assumed as inert gases in the presence of CO and H$_2$ at a high temperature, which is wrong from a thermodynamic consideration. In a well-mixed reactor, the combustion products CO$_2$ and H$_2$O should participate freely in the reactions. However in a real reactor, there is incomplete mixing between combustion products and raw materials. It is much better to introduce a mixing factor, which characterizes the reactor design, than to assume the combustion products are inert. The initial gas components are shown in TABLE 2.6.

<table>
<thead>
<tr>
<th>Component</th>
<th>C$_6$H$_6$</th>
<th>O$_2$</th>
<th>H$_2$O</th>
<th>CO$_2$</th>
<th>N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc., mol/L</td>
<td>$3.05 \times 10^{-4}$</td>
<td>$4.15 \times 10^{-4}$</td>
<td>$7.86 \times 10^{-4}$</td>
<td>$5.00 \times 10^{-4}$</td>
<td>$4.64 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
FIGURE 2.3.1 Concentration profile of initial reactants

FIGURE 2.3.2 Concentration profile of products

FIGURE 2.3.3 Concentration profile of key intermediate species

FIGURE 2.3.4 Concentration profile of particle classes A-J

FIGURE 2.3 Concentration profile during benzene pyrolysis and oxidation (Ivie and Forney, 1988)
2.3 REVIEW OF COAL CONVERSION TECHNOLOGY

2.3.1 COAL CHARACTERIZATION

The typical coal is a heterogeneous mixture of organics and inorganics. The organic portion consists of a series of aromatic/hydroaromatic clusters containing an average of 2~5 rings per cluster and joined together by methylene linkage, 1~3 carbon atoms in length (FIGURE 2.4). This structure promotes a complex interlocking molecular structure similar to many organic polymers. The clusters are only loosely connected by aliphatic linkages. During heat treatment these bonds are severed, the lower weight hydrocarbons (including hydrogen, methane, benzene, etc.) are released, and these lower weight hydrocarbons play an important role in the formation of carbon black.

FIGURE 2.4 Structure of coal (Given, 1960)
Because of the complex nature of the clusters and the linkage, it is not possible to represent coal exactly. Instead, the ultimate analysis and proximate analysis are often used. The ultimate analysis can be used to construct an empirical formula for coal. However, it bears no information about the products/distributions in a coal conversion process. On the other hand, the proximate analysis can predict the amount of water, volatile, carbon and ash produced under certain conditions.

2.3.2 COAL PYROLYSIS

\[
\text{Coal} \rightarrow \text{Char} + \text{Volatile matter} + \text{Water} \tag{2.29}
\]

The pyrolysis of coal is generally defined as the thermal decomposition of coal in the absence of air or other added substances. It occurs with the production of gas, liquor (low molecular weight liquids), tar (high molecular weight liquids) and char (coke). The gas, liquor and tar are called volatile matter. The amount of volatile matter released from coal depends upon the rate of heating. The volatile yields for conditions of rapid heating ($10^2 - 10^4 \, \text{K/sec.}$) are usually in excess of those obtained from proximate analysis (where the heating rate is less than $10^2 \, \text{K/sec.}$). Anthony and Howard (1976) observed that it could be 36% more. Besides the rate of heating, the amount of volatile matter evolved during coal pyrolysis also depends on the final pyrolysis temperature, the particle residence time, and coal rank. Not only does the amount of volatile matter released vary with the heating rate, but its composition changes as well. Anthony (1976) observed the
liquid to gas ratio varies from 1 to 3. Some information on composition was reported by Speight (1994), and is reproduced here (TABLE 2.7 and TABLE 2.8). TABLE 2.7 shows the gas composition and yields at different pyrolysis temperatures. TABLE 2.8 shows the typical light oil product from the high temperature pyrolysis. These two tables tell that methane is the dominant component in the gas products through out all the temperatures, and benzene is the dominant component in the liquid products.

TABLE 2.7 Gas composition at different coal pyrolysis temperatures (Speight, 1994)

<table>
<thead>
<tr>
<th>Gas composition and yields, (v%)</th>
<th>Temperature of carbonization (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500</td>
</tr>
<tr>
<td>CO₂</td>
<td>5.7</td>
</tr>
<tr>
<td>Unsaturates</td>
<td>3.2</td>
</tr>
<tr>
<td>CO</td>
<td>5.8</td>
</tr>
<tr>
<td>H₂</td>
<td>20.0</td>
</tr>
<tr>
<td>CH₄</td>
<td>49.5</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>14.0</td>
</tr>
<tr>
<td>Yield (m³/tonne)</td>
<td>62.3</td>
</tr>
</tbody>
</table>

TABLE 2.8 Representative composition of a light oil from the high-temperature carbonization of coal (Speight, 1994)

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Amount, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>61</td>
</tr>
<tr>
<td>Toluene</td>
<td>23</td>
</tr>
<tr>
<td>o-Xylene + m-Xylene + p-Xylene</td>
<td>10</td>
</tr>
<tr>
<td>Styrene</td>
<td>2</td>
</tr>
<tr>
<td>Miscellaneous (aromatic, aliphatic, and olefins)</td>
<td>4</td>
</tr>
</tbody>
</table>
Many authors (Anthony, 1975; Subberg, 1978; Solomon, 1983; Merrick, 1987) have approximated the overall process as a first-order decomposition occurring uniformly throughout the particle. Thus, the rate of coal pyrolysis is expressed as:

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

(2.30)

$V^*$ represents the effective volatile content of the coal, and as discussed before, it is significantly larger than the volatile matter determined by proximate analysis. According to Anthony and Howard (1976), the average ratio ($V^*/V$) is 1.1. As for $k = k_0 \exp(-E/RT)$, there is little agreement on the observed rate constants, with several orders of magnitude discrepancy at a given temperature. Apparent activation energies range from 2 to 50 kcal/mole. The frequency factor ($k_0$) varies from $10^2$ to $10^{10}$ s$^{-1}$.

2.3.3 CARBON BLACK PROCESS FROM COAL

The formation of carbon black form coal involves an initial pyrolysis of the coal to char, tar, and gaseous hydrocarbons. These tar and gaseous hydrocarbons subsequently react to form carbon black.

Many patents and research data (Johnson, 1966; Iyengar, 1971; Cheng, 1976, 1980, 1981; Chen & Savage, 1986, 1992) discussed the possibility of producing carbon black from coal, but little experimental data were available. Chen and Savage (1992) reported some experimental results.

FIGURE 2.5 shows their experimental apparatus. Coal was fed into an isothermal reactor with oxygen, Carbon black, synthesis gas and char were produced.
FIGURE 2.5 Experimental Apparatus
The proximate and ultimate analysis of coal is reproduced in TABLE 2.9.
The experimental results are summarized in TABLE 2.10 and TABLE 2.11.

**TABLE 2.9** Proximate and ultimate analysis of coal (dry basis, wt%)
Clarion 4A (Ohio) (Chen and Savage, 1992)

<table>
<thead>
<tr>
<th>Volatile</th>
<th>Fixed Carbon</th>
<th>Ash</th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Oxygen</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>46</td>
<td>12</td>
<td>70</td>
<td>5</td>
<td>9</td>
<td>3</td>
</tr>
</tbody>
</table>

**TABLE 2.10** Experimental results for Clarion 4A coal using an isothermal reactor
(Chen and Savage, 1992)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1150</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Coal (kg/hr)</td>
<td>1.9</td>
</tr>
<tr>
<td>Oxygen (liter/min)</td>
<td>5</td>
</tr>
<tr>
<td>Water (cc/min)</td>
<td>2</td>
</tr>
<tr>
<td>Nitrogen (liter/min)</td>
<td>5</td>
</tr>
<tr>
<td>Product Gas (liter/min)</td>
<td>25</td>
</tr>
<tr>
<td>H₂ (%)</td>
<td>48</td>
</tr>
<tr>
<td>N₂ (%)</td>
<td>20</td>
</tr>
<tr>
<td>CH₄ (%)</td>
<td>5</td>
</tr>
<tr>
<td>CO (%)</td>
<td>26</td>
</tr>
<tr>
<td>CO₂ (%)</td>
<td>1</td>
</tr>
<tr>
<td>Carbon black (kg/hr)</td>
<td>0.38</td>
</tr>
<tr>
<td>C (%)</td>
<td>95</td>
</tr>
<tr>
<td>H (%)</td>
<td>1</td>
</tr>
<tr>
<td>O (%)</td>
<td>0</td>
</tr>
<tr>
<td>S (%)</td>
<td>2</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>1</td>
</tr>
<tr>
<td>Char (kg/hr)</td>
<td>0.97</td>
</tr>
<tr>
<td>C</td>
<td>72</td>
</tr>
<tr>
<td>H</td>
<td>1</td>
</tr>
<tr>
<td>O</td>
<td>0</td>
</tr>
<tr>
<td>S</td>
<td>3</td>
</tr>
<tr>
<td>Ash</td>
<td>23</td>
</tr>
</tbody>
</table>
2.3.4 SUMMARY OF COAL PYROLYSIS PARAMETERS

As discussed in this review, the main uncertainty in the generation of carbon black from coal is from coal pyrolysis. Therefore, it is necessary to compile a set of data to use. TABLE 2.12 shows some reasonable values that can be used.

TABLE 2.12 The parameters chosen in coal pyrolysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio of effective volatile ($V^e$) and proximate volatile ($VM$)</td>
<td>1.1</td>
</tr>
<tr>
<td>Volatile matter distribution, wt%</td>
<td></td>
</tr>
<tr>
<td>Liquid ($C_6H_6$)</td>
<td>64</td>
</tr>
<tr>
<td>Gas</td>
<td>24</td>
</tr>
<tr>
<td>Chemical water</td>
<td>12</td>
</tr>
<tr>
<td>Gas Component, vol%</td>
<td></td>
</tr>
<tr>
<td>$CO_2$</td>
<td>10</td>
</tr>
<tr>
<td>$CO$</td>
<td>24</td>
</tr>
<tr>
<td>$H_2$</td>
<td>2</td>
</tr>
<tr>
<td>$CH_4$</td>
<td>46</td>
</tr>
<tr>
<td>Others ($C_2H_6$)</td>
<td>18</td>
</tr>
</tbody>
</table>
CHAPTER 3 MATHEMATICAL MODELING

3.1 MODEL'S ELEMENTS AND PREMISES

A mathematical model is presented in this chapter. This model is comprehensive in that it can predict carbon black generation form methane, benzene, as well as coal. The main purpose is to predict carbon black from coal.

An isothermal, plug-flow model is employed in this work as depicted in FIGURE 3.1. The raw material, coal, enters from one end of the reactor, and the product, carbon black, exits from the other end of the reactor. The independent variable for the calculation is the reaction time, which is related to the flow of the mixture and the length of reactor.

\[
\begin{align*}
N_2, O_2 & \rightarrow \\
H_2O, CO_2 & \rightarrow \\
COAL & \rightarrow 
\end{align*}
\]

FIGURE 3.1 Schematic diagram of reactor elements in the model

3.2 DETAILED COMPONENTS IN THIS MODEL

This section describes the detailed components in the model.

(1) **Mixing:** characterizing the reactor

(2) **Coal pyrolysis:** producing methane and benzene and other chemicals
(3) **Gas phase reactions**: producing radical fragments on which nucleation may begin

(4) **Nucleation**: producing the first-class particle by nucleus and growth species

(5) **Coagulation**: particles may grow by coagulation between different particles

(6) **Growth**: particles may grow to a bigger particle by adding the growth species

(7) **Oxidation**: particles may shrink to smaller particles by oxidation with oxidizing materials such as OH

3.2.1 MIXING

A mixing factor, \( m \), is introduced in this study to characterize the reactor mixing. For typical commercial reactors, the energy for carbon black reaction is provided internally by the hot combustion product produced by burning some gas or liquid fuel. The same gas or liquid may serve as raw material but they enter the reactor subsequently through different ports. The reactor design usually minimizes the mixing, therefore the reactions, between combustion products and raw materials, are minimized. Otherwise, carbon monoxide would be the forward product instead of carbon black. Therefore it is convenient to use a mixing factor to represent the fraction of the combustion product that participates in the carbon black reaction. This mixing factor is a characteristic of an individual reactor and can be determined experimentally. The value of the mixing factor is usually close to 0. However, for some reactors, it could be 1.
3.2.2 COAL PYROLYSIS

As discussed in the previous chapter, coal pyrolysis is a very complex chemical reaction. There are uncertainties in the rate of the reaction, the amount of volatile matter produced as well as the distribution of tar and gas. There are also uncertainties about where in the reactor pyrolysis starts and where it is completed. In this work, completed pyrolysis is assumed to simplify the calculation. In other words, coal is devolatilized to C6H6, H2O, CH4, C2H6, CO, CO2, H2, according to TABLE 2.12.

3.2.3 GAS PHASE REACTIONS

The gas phase reactions convert the volatile matters produced from coal to nuclei of carbon black. A total of fifty-four chemical reactions are considered. They are grouped into methane pyrolysis, C1 and C2 oxidation, benzene pyrolysis and oxidation, and H-O balance reactions. All the gas reactions are represented by the simple equation: 

\[-r = A\exp(-E/RT) C^n\]

The parameters in the equations are listed in appendix A.

3.2.3.1 METHANE PYROLYSIS

A total of eleven chemical reactions are used to describe the generation of free radicals such as C2, C2H, C2H2, C2H3, C2H4, and C2H5 from CH4:

\[\text{CH}_4 \rightleftharpoons \text{•CH}_3 + \text{•H} \quad (3.1)\]

\[\text{CH}_4 + \text{•H} \rightleftharpoons \text{•CH}_3 + \text{H}_2 \quad (3.2)\]
Comparing with the reaction set Jensen (1976) used, we added two reactions: Eq.3.4 and Eq.3.7. The reason for the difference is that what Jensen used was a "minimum set". In the literature search, we found these two reactions are also important.

3.2.3.2 C1 AND C2 OXIDATION

When oxygen is involved in the reaction, the reactions would be not as simple as pyrolysis. The major reaction pathways in aliphatic hydrocarbon combustion have been studied extensively. Warnatz (1984) examined the combustion mechanisms of simple aliphatics by computer kinetic modeling. The dominant route is via C1-species, but the parallel C2-pathway is also important.
\[
\begin{align*}
\text{CH}_4 + \cdot \text{OH} & \rightleftharpoons \cdot \text{CH}_3 + \text{H}_2\text{O} & (3.12) \\
\text{CH}_4 + \cdot \text{HO}_2 & \rightleftharpoons \cdot \text{CH}_3 + \text{H}_2\text{O}_2 & (3.13) \\
\text{CH}_4 + \text{O} & \rightleftharpoons \cdot \text{CH}_3 + \cdot \text{OH} & (3.14) \\
\cdot \text{CH}_3 + \cdot \text{OH} & \rightleftharpoons \text{CH}_2\text{O} + \text{H}_2 & (3.15) \\
\cdot \text{CH}_3 + \text{O} & \rightleftharpoons \text{CH}_2\text{O} + \cdot \text{H} & (3.16) \\
\text{CH}_2\text{O} + \cdot \text{OH} & \rightleftharpoons \cdot \text{HCO} + \text{H}_2\text{O} & (3.17) \\
\text{CH}_2\text{O} + \cdot \text{H} & \rightleftharpoons \cdot \text{HCO} + \text{H}_2 & (3.18) \\
\text{CH}_2\text{O} + \text{O} & \rightleftharpoons \cdot \text{HCO} + \cdot \text{OH} & (3.19) \\
\cdot \text{HCO} + \cdot \text{OH} & \rightleftharpoons \text{CO} + \text{H}_2\text{O} & (3.20) \\
\cdot \text{HCO} + \cdot \text{H} & \rightleftharpoons \text{CO} + \text{H}_2 & (3.21) \\
\cdot \text{HCO} + \text{O} & \rightleftharpoons \text{CO} + \cdot \text{OH} & (3.22) \\
\text{CO} + \cdot \text{OH} & \rightleftharpoons \text{CO}_2 + \cdot \text{H} & (3.23) \\
\text{CO} + \cdot \text{HO}_2 & \rightleftharpoons \text{CO}_2 + \cdot \text{OH} & (3.24) \\
\text{CO}_2 + \text{O} & \rightleftharpoons \text{CO} + \text{O}_2 & (3.25) \\
\text{C}_2\text{H}_6 + \cdot \text{OH} & \rightleftharpoons \cdot \text{C}_2\text{H}_5 + \text{H}_2\text{O} & (3.26) \\
\text{C}_2\text{H}_6 + \text{O} & \rightleftharpoons \cdot \text{C}_2\text{H}_5 + \cdot \text{OH} & (3.27) \\
\cdot \text{C}_2\text{H}_5 + \text{O}_2 & \rightleftharpoons \text{C}_2\text{H}_4 + \cdot \text{HO}_2 & (3.28) \\
\text{C}_2\text{H}_4 + \text{O} & \rightleftharpoons \cdot \text{CH}_3 + \cdot \text{HCO} & (3.29) \\
\text{C}_2\text{H}_4 + \cdot \text{OH} & \rightleftharpoons \cdot \text{C}_2\text{H}_3 + \text{H}_2\text{O} & (3.30) \\
\cdot \text{C}_2\text{H}_3 + \text{O}_2 & \rightleftharpoons \cdot \text{HCO} + \text{H}_2\text{O} & (3.31)
\end{align*}
\]
3.2.3.3 BENZENE PYROLYSIS AND OXIDATION

A gas phase reversible chemical reaction scheme was designed to describe the production of initial nucleus species such as \( \text{C}_6\text{H}_5 \) and \( \text{C}_{12}\text{H}_{10} \) from \( \text{C}_6\text{H}_6 \). Comparing with Ivie and Forney (1988), we considered all reactions to be reversible, and we also added some intermediate reactions to connect C6 and C2.

\[
\begin{align*}
\text{C}_2\text{H}_2 & + \text{O} \rightleftharpoons \cdot\text{C}_2\text{H} + \cdot\text{OH} \\
\cdot\text{C}_2\text{H} & + \text{O} \rightleftharpoons \text{CO} + \cdot\text{CH} \\
\text{CH}_2 & + \text{O} \rightleftharpoons \text{CO} + \text{H}_2 \\
\text{CH}_2 & + \cdot\text{H} \rightleftharpoons \cdot\text{CH} + \text{H}_2 \\
\cdot\text{CH} & + \text{O} \rightleftharpoons \cdot\text{CO} + \text{H}
\end{align*}
\]

\( (3.32) \)  \( (3.33) \)  \( (3.34) \)  \( (3.35) \)  \( (3.36) \)

\[
\begin{align*}
\text{C}_6\text{H}_6 & \rightleftharpoons \cdot\text{C}_6\text{H}_5 + \cdot\text{H} \\
\text{C}_6\text{H}_6 & + \cdot\text{H} \rightleftharpoons \cdot\text{C}_6\text{H}_5 + \text{H}_2 \\
\text{C}_6\text{H}_6 & + \cdot\text{C}_6\text{H}_5 \rightleftharpoons \text{C}_{12}\text{H}_{10} + \cdot\text{H} \\
\text{C}_{12}\text{H}_{10} & \rightleftharpoons 2\cdot\text{C}_6\text{H}_5 \\
\cdot\text{C}_6\text{H}_5 & \rightleftharpoons \text{C}_2\text{H}_2 + \cdot\text{C}_4\text{H}_3 \\
\text{C}_6\text{H}_6 & \rightleftharpoons \text{C}_2\text{H}_2 + \text{C}_4\text{H}_4 \\
\cdot\text{C}_4\text{H}_3 & \rightleftharpoons \cdot\text{C}_2\text{H} + \text{C}_2\text{H}_2 \\
\text{C}_4\text{H}_4 & \rightleftharpoons \cdot\text{C}_2\text{H} + \cdot\text{C}_2\text{H}_3 \\
\text{C}_6\text{H}_6 & + \text{O}_2 \rightleftharpoons \cdot\text{C}_6\text{H}_5 + \cdot\text{HO}_2
\end{align*}
\]

\( (3.37) \)  \( (3.38) \)  \( (3.39) \)  \( (3.40) \)  \( (3.41) \)  \( (3.42) \)  \( (3.43) \)  \( (3.44) \)  \( (3.45) \)
In the high-temperature regime, however, the following reactions (3.50 - 3.54) control the relative concentration of O, OH, and H.

\[
\begin{align*}
C_6H_6 + O & \rightleftharpoons C_6H_5 + OH \\
C_6H_6 + OH & \rightleftharpoons C_6H_5 + H_2O \\
C_6H_6 + HO_2 & \rightleftharpoons C_6H_5 + H_2O_2 \\
C_6H_5 + O_2 & \rightleftharpoons 2CO + C_2H_2 + C_2H_3
\end{align*}
\]

3.2.3.4 H-O BALANCE

Benzene and methane pyrolysis are considered to be the pyrolysis reaction sets which provide a reasonable description of the formation of growth species (C_{2}, C_{2}H, C_{2}H_{2}, C_{2}H_{3}, C_{4}H_{3}, C_{4}H_{4}) and the initial nucleus species (C_{2}, C_{2}H, C_{6}H_{5}, C_{12}H_{10}). At high temperatures (>1000 K) the radicals H, O, and OH become responsible for chain branching; C1 and C2 oxidation described this; the H-O reactions balance H, O, OH in the reactor.
3.2.4 NUCLEATION

Candidates for the initial nucleus in which coagulation and growth may begin are C₂, •C₂H and •C₆H₅, C₁₂H₁₀; It is reasonable to suggest that C₂, •C₂H, C₂H₂, •C₂H₃, •C₄H₃, C₄H₄ are growth species. The particle classification is modified based on Jensen's set as shown in TABLE 3.1. Particle class "A" remains the same as Jensen's. The rest of the particle classes have smaller diameters than the ones used by him. However, for most of the particle classes, the diameter of Pᵢ is the same as that of Pᵢ₊₁ used by Jensen. Therefore, the results can still be compared.

TABLE 3.1 Particle radii (particles are taken to be spherical)

<table>
<thead>
<tr>
<th>Particles</th>
<th>Radius, (nm)</th>
<th>Carbon atoms per particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pₐ</td>
<td>0.2</td>
<td>4</td>
</tr>
<tr>
<td>Pₐ</td>
<td>0.32</td>
<td>14</td>
</tr>
<tr>
<td>P₉</td>
<td>0.49</td>
<td>50</td>
</tr>
<tr>
<td>P₉</td>
<td>0.95</td>
<td>360</td>
</tr>
<tr>
<td>P₉</td>
<td>2.3</td>
<td>5080</td>
</tr>
<tr>
<td>P₉</td>
<td>5.7</td>
<td>7.8 × 10⁴</td>
</tr>
<tr>
<td>P₉</td>
<td>15</td>
<td>1.44 × 10⁶</td>
</tr>
<tr>
<td>P₉</td>
<td>32</td>
<td>1.32 × 10⁷</td>
</tr>
<tr>
<td>P₉</td>
<td>63</td>
<td>1.06 × 10⁸</td>
</tr>
<tr>
<td>P₉</td>
<td>150</td>
<td>1.47 × 10⁹</td>
</tr>
<tr>
<td>P₉</td>
<td>380</td>
<td>2.32 × 10¹⁰</td>
</tr>
<tr>
<td>P₉</td>
<td>790</td>
<td>2.07 × 10¹¹</td>
</tr>
<tr>
<td>P₉</td>
<td>1600</td>
<td>1.66 × 10¹²</td>
</tr>
<tr>
<td>P₉</td>
<td>3800</td>
<td>2.31 × 10¹³</td>
</tr>
</tbody>
</table>
The formation of the first two-class particles \((P_A, P_B)\) is considered as nucleation reaction. A simple assumption is this: initial nucleus and growth species react to become \(P_A\) (or \(P_B\)), no other particles were formed through these reactions. Based on \(P_A\) (or \(P_B\)), \(P_B\) (or \(P_C\)) is formed, and so on. Nucleation reactions will be considered as irreversible reactions.

\[
N + G \rightarrow P_A \text{ or } B \tag{3.55}
\]

Where, \(N\) is initial nucleus \((C_2, C_2H, C_6H_5, C_{12}H_{10})\);

\(G\) is growth species \((C_2, C_2H, C_2H_2, C_2H_3, C_4H_3, C_4H_4)\);

To simplify the reactions, we divided growth species \(G\) into C2 group and C4 group, therefore, we have six reactions for nucleation.

\[
\begin{align*}
C_2 + C_2H &\rightarrow P_A \tag{3.56.1} \\
C_2H + C_2H_2 &\rightarrow P_A \tag{3.56.2} \\
C_6H_5 + \text{C2 group (or C4 group)} &\rightarrow P_B \tag{3.56.3} \\
C_{12}H_{10} + \text{C2 group (or C4 group)} &\rightarrow P_B \tag{3.56.4}
\end{align*}
\]

3.2.5 COAGULATION

After the comparison and research on the coagulation rate formula (Jensen, 1974; Forney, 1994; Fuch, 1989), we chose Forney's formula (Eq.2.3) to calculate particle
coagulation rate constants. All particles except the largest were permitted to coagulate irreversibly with all others via inclusion of rate terms for processes of type.

\[ v \, P_i + P_j \rightarrow P_{j+1} \]  \hspace{1cm} (3.57)

Where \(i, j\) run alphabetically from A to N, \(v\) is the number of class \(P_i\) particle determined from carbon balance. There are ninety-one coagulation reactions that are considered for coagulation.

3.2.6 GROWTH

The reactions between growth species and carbon black particles were considered in this section. A series of particle growth terms analogous to those for coagulation may then be written for the irreversible conversion:

\[ P_i + v \, C_2H_2 \rightarrow P_{i+1} \]  \hspace{1cm} (3.58)

with reaction rate:

\[ -d[C_2H_2]/dt = d[H]/dt = \kappa_{ai}[P_i][C_2H_2] \]  \hspace{1cm} (3.59)

\[ -d[P_i]/dt = d[P_{i+1}]/dt = \kappa_{bi}[P_i][C_2H_2] \]  \hspace{1cm} (3.60)

where \((n_{i+1} - n_i)\kappa_{bi} = 2\kappa_{ai}\) for growth species \((C_2, C_2H, C_2H_2, C_2H_3)\), and \((n_{i+1} - n_i)\kappa_{bi} = 4\kappa_{ai}\) for growth species \((C_4H_3\) and \(C_4H_4)\).

There are twenty-six reactions that are considered as particle growth reactions. The rate constants were calculated following the coagulation rate constant formula.
3.2.7 OXIDATION

Oxidation of particles may be treated in a manner analogous to that used for the coagulation process (Eq.2.28). We have detailed discussion about this reaction in the previous chapter (2.2.2.4 OXIDATION), and we used the literature results about this reaction. There are fourteen particle classes in our study, which means there are fourteen oxidation reactions involved.

3.3 COMPUTER CODE DEVELOPMENT

The model described above contains one coal pyrolysis, fifty-four chemical reactions, six nucleation reactions, ninety-one coagulation reactions, twenty-six particle growth reactions and fourteen oxidation reactions. Therefore it involves the solving of a total one hundred ninety-two nonlinear, stiff ordinary differential equations. To solve those ODEs, an IMSL subroutine DIVPG (Double-precision Initial Value Problem for ordinary differential equations using an Adams or Gear method) was used.

A FORTRAN program was written for this model as attached in Appendix B. The flow sheet is shown in FIGURE 3.2. The program was run on a UNIX machine. Because of the size and stiffness of the program, it generally takes twenty-four to forty-eight hours to make one run. The results are presented in the next chapter.
Main() starts

Initialization

Using ISML subroutine DIVPAG to get next values for all the parameters

Error > 1E-6

YES

NO

Output data

Time > Tmax
OR
Length > Lmax

YES

NO

Program

FIGURE 3.2 The computer flow sheet of this model
CHAPTER 4 RESULTS AND DISCUSSION

The computer code developed in the previous chapter is employed here to calculate results for comparison. The validation of the computer code is first checked by comparing the calculated results with those from Jensen's code for carbon black from methane. It is then checked with Ivie and Forney's for carbon black from benzene. The program is then used to calculate carbon black generated from coal that is compared to experimental data. Finally the effect of coal volatile matter, volatile distribution and temperature are reported.

4.1 CARBON BLACK FROM METHANE PYROLYSIS

Using the same initial concentrations and the same temperature as used by Jensen (See FIGURE 2.1), the species generated in methane pyrolysis are calculated and shown in FIGURE 4.1, which are very similar to FIGURE 2.1 obtained by Jensen. Most concentrations are very close, some of them (CH₄, H₂, H, CH₃, C₂H₅, C₂H₃) are almost identical. The differences are too little to be noticed. The small differences result from different chemical reactions, particle classes and rate constants. The reason for the similarity is because the feed contains only methane, hydrogen and no oxygen; therefore our consideration for benzene reactions and oxidation has no effect on the result. The effective reactions left are methane pyrolysis and carbon nucleation, which are similar to those in Jensen's model.
FIGURE 4.1 Species concentration during methane pyrolysis
4.2 CARBON BLACK FROM BENZENE OXIDATION

The computer program is then employed to calculate the species generated in benzene oxidation for comparison.

As pointed out in the previous chapter, one of the differences between Ivie and Forney's model and this model is that we introduced a mixing parameter to characterize the mixing between combustion products and raw materials in a real reactor. Therefore, the comparison will be done in two parts. In the first part, the mixing parameter is set to zero, this actually means that the combustion products do not participate in the reactions, as Ivie and Forney assumed in their paper.

The results are shown in FIGURE 4.2 and FIGURE 4.3. In FIGURE 4.2, we present the particle concentration at different reaction times. The tendency is the total particle size is increased with the increasing of time. At 4 milliseconds, the dominant particle class is $P_G$ particle; at 40 milliseconds, the dominant particle class is $P_H$ particle; and at 600 milliseconds, the dominant particle class becomes $P_I$ particle.

In FIGURE 4.3, we present the dominant gas components. Comparing with FIGURE 2.3.2, one can see that predictions of carbon monoxide concentration are very close. However our prediction of the hydrogen concentration is about the same as that of carbon monoxide, which is one order of magnitude higher than that predicted by Ivie and Forney. Although, a direct comparison with the actual experimental data is not available, our results are more similar to the data obtained in a typical industrial operation (Lewis, 1974). Another difference is that oxygen declines more gradually in our model.
FIGURE 4.2 Particle distribution at different reaction time (m=0)

FIGURE 4.3 Gas species concentration during partial combustion of benzene (m=0)
Now, we assume complete mixing of combustion products with feedstock by setting the mixing factor to 1. The results are shown in FIGURE 4.4 and FIGURE 4.5. By comparing FIGURE 4.4 and 4.5 with FIGURE 4.2 and 4.3, we conclude that the effect of mixing is a decrease of carbon and carbon dioxide and an increase of carbon monoxide.

FIGURE 4.6 compares the calculated particle size with the mixing factors set to 0 and 1. It can be seen that the particle size decreases significantly because of the mixing.

TABLE 4.1 summarizes the experimented and calculated data at a reaction time of 10 ms. When comparing it to the experimental data, the prediction by this model is slightly better than that by Ivie and Forney. It also shows that mixing improves the prediction for both carbon black size and carbon monoxide concentration.
FIGURE 4.5 Gas species concentration during partial combustion of benzene ($m=1$)

FIGURE 4.6 Mass average particle size during partial combustion of benzene
4.3 CARBON BLACK FROM COAL

After comparing the calculated results for carbon black generated from methane and benzene, we proved that our model is as good if not better than the previously reported models. Now we proceed to calculate the carbon black generated from coal. The calculated results are compared with the experimental data reported by Chen and Savege (1992).

4.3.1 COMPRISION WITH EXPERIMENTAL DATA

The calculated results on coal process are shown in FIGURE 4.7 through FIGURE 4.12. Three figures are used to present the calculated results for gas phase species. FIGURE 4.7 shows dominant gas species. The major components are H₂, CH₄, CO and CO₂. The others are orders of magnitude smaller. FIGURE 4.8 displays aromatics (C₆ and C₁₂). Some oxygen compounds are depicted in FIGURE 4.9. The experimental and modeling results are compared in TABLE 4.2.

### TABLE 4.1 Experimental and calculated results at 10 ms

<table>
<thead>
<tr>
<th></th>
<th>Experimental</th>
<th>Ivie's result</th>
<th>This model, mixing=0</th>
<th>This model, mixing=1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass avg. particle dia., nm</td>
<td>66 ± 10</td>
<td>73</td>
<td>72</td>
<td>64</td>
</tr>
<tr>
<td>Particle conc., no./cm³</td>
<td>4.5 ± 0.6×10¹⁰</td>
<td>3.7×10¹⁰</td>
<td>3.8×10¹⁰</td>
<td>3.5×10¹⁰</td>
</tr>
<tr>
<td>CO conc., mol/L</td>
<td>7.9 ± 0.5×10⁻⁴</td>
<td>6.0×10⁻⁴</td>
<td>5.7×10⁻⁴</td>
<td>6.8×10⁻⁴</td>
</tr>
</tbody>
</table>
From TABLE 4.2, one can see that the experimental and modeling results are close to each other.

FIGURE 4.10 shows the concentration profiles of all different particle classes as a function of time. They are recalculated to show the yield of carbon black in FIGURE 4.11 and the average particle size in FIGURE 4.12. It shows a self-preserving tendency, which was exactly observed in the literature. At 1-second reaction time, the particle size is 225 nm, which is comparable to the experimental value of 200 nm.

It can be concluded that the calculated results are very close to the experimental data. Until now, our model has been successfully applied to all the processes using methane, benzene, and coal (Clarion 4A, Ohio) as its feedstock.
FIGURE 4.7  Gas species concentration vs. time

FIGURE 4.8  Aromatics concentration vs. time
FIGURE 4.9 Oxygen concentration vs. time

FIGURE 4.10 Particle concentration vs. time
FIGURE 4.11 Yield of carbon black vs. time

FIGURE 4.12 Mass average particle size vs. time
4.3.2 SENSITIVITY STUDY

As we mentioned in the literature review, the composition of coal is very complicated. The effects of the coal properties, such as volatile matters and tar/water/gas ratio in volatile matter, on coal carbon black are far from certain. It is important to estimate their effects on carbon black generation. The temperature is also investigated. The following sections present these sensitivity studies.

4.3.2.1 VOLATILE MATTER

Volatile matter is one of important properties of coal. It directly indicates the amount that can be released in coal pyrolysis. The amount of volatile matter varies dramatically according to the pyrolysis conditions. In order to study the effect of volatile matter, several values of effective volatile matter are chosen accordingly.

The reported volatile matter for Clarion 4A coal is 42%. Under fast heating, the effective volatile matter produced may increase to 55%. Therefore, the computer program was run at different volatile matters of 42%, 47% and 52%.

The results are shown in FIGURE 4.13 and FIGURE 4.14. At the end of one second, when the volatile matter increases from 42% to 52%, the particle diameter increases by about 10% (FIGURE 4.13). The yield of carbon black increases by about 25% (FIGURE 4.14). The carbon black yield is sensitive to volatile as we expected.
FIGURE 4.13 Mass average particle size vs. time

FIGURE 4.14 Yield of carbon black vs. time
4.3.2.2 TAR-GAS-WATER RATIO

The tar, gas and water compose the volatile matter. The ratio between these components is another uncertain issue. According to Anthony (1976), we selected three different ratios, which will cover most ratio range among tar, gas, and water, to test the effect on carbon black generation.

1) tar/gas/water = 0.70/0.21/0.09;
2) tar/gas/water = 0.64/0.24/0.12;
3) tar/gas/water = 0.58/0.26/0.16;

The results are showed in FIGURE 4.15 and 4.16. FIGURE 4.15 compares the difference of particle size at different tar-gas-water ratio under the same effective volatile matter (47%). The trends for these curves are the higher the tar is, the bigger the particle size is. At one second, from the lowest tar ratio to the highest tar ratio, the particle diameter size increases by about 10%. It seems that benzene (or tar portion) has more influence than methane (or gas portion) does. From FIGURE 4.16, the yield of carbon black increases by about 25%, which has the similar trend as FIGURE 4.14 does. The conclusion we got here is similar to the previous section: the carbon black yield is sensitive to volatile matter as we expected.
FIGURE 4.15 Mass average particle size vs. time

FIGURE 4.16 Yield of carbon black vs. time
Temperature is another important factor that affects the carbon black process. The literature search showed that it is one of the most important factors, this is also true in our model. FIGURE 4.17 showed our modeling results at various temperatures. The results have the same general trends as Ivie and Forney's. Interestingly enough is FIGURE 4.18: the yield of carbon black vs. time. The higher the reaction temperatures are, the lower the yields are, which reminds us that at high temperature, the oxidation is more important, and removes more carbon black.

In conclusion, both properties of coal (effective volatile and ratio of tar/water/gas) and the temperature are important in carbon black generation. The trends of these parameters' effects are consisted with the literatures.
FIGURE 4.17 Effect of temperature on mass average particle size

FIGURE 4.18 Effect of temperature on yield of carbon black
CHAPTER 5 CONCLUSION AND FUTURE WORK

5.1 CONCLUSION

This research successfully modeled carbon black production using coal as a feedstock. The calculated carbon black size and gas compositions are close to the experimental data.

This model can be used to simulate the carbon black production from methane or any other gas feedstock. It can also be used to simulate the carbon black production from benzene or the other liquid feedstock such as petroleum tars or coal tars.

The effects of coal properties such as total effective volatile matter and tar-gas-water ratio in volatile matter were investigated. Their effects on carbon black yield are significant, however their effects on carbon black size are relatively small. The reaction temperature significantly affects carbon black particle size and yield, particularly at short reaction time.

5.2 FUTURE WORK

This work assumed instant coal pyrolysis, the pyrolysis rate should be considered in the future. This work considered the isothermal reactor, the heat transfer should be considered in the future. This work studied only one important property of carbon black: size and size distribution. In the future, the model can be extended to study the other two properties, surface area and structure.
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### APPENDIX A. CHEMICAL RATE CONSTANTS

#### TABLE A-1 Chemical reaction forward rate constants

<table>
<thead>
<tr>
<th>Reaction</th>
<th>LogA (cm³/mols)</th>
<th>n</th>
<th>Eₚ(KJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I). Methane pyrolysis</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1 CH₄ → CH₃ + H</td>
<td>14.0</td>
<td>0.0</td>
<td>101.9</td>
</tr>
<tr>
<td>3.2 CH₄ + H → CH₃ + H₂</td>
<td>14.1</td>
<td>0.0</td>
<td>11.9</td>
</tr>
<tr>
<td>3.3 C₂H₆ → CH₃ + CH₃</td>
<td>19.1</td>
<td>-1.0</td>
<td>88.3</td>
</tr>
<tr>
<td>3.4 C₂H₆ + CH₃ → C₂H₅ + CH₄</td>
<td>-0.30</td>
<td>4.0</td>
<td>8.3</td>
</tr>
<tr>
<td>3.5 C₂H₆ + H → C₂H₅ + H₂</td>
<td>2.7</td>
<td>3.5</td>
<td>5.2</td>
</tr>
<tr>
<td>3.6 C₂H₅ → C₂H₄ + H</td>
<td>13.6</td>
<td>0.0</td>
<td>38.0</td>
</tr>
<tr>
<td>3.7 C₂H₅ + CH₃ → C₂H₄ + CH₄</td>
<td>17.5</td>
<td>0.0</td>
<td>35.6</td>
</tr>
<tr>
<td>3.8 C₂H₄ + H → C₂H₃ + H₂</td>
<td>13.8</td>
<td>0.0</td>
<td>6.0</td>
</tr>
<tr>
<td>3.9 C₂H₃ + Ar → C₂H₂ + H + Ar</td>
<td>13.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3.10 C₂H₂ + H → C₂H + H₂</td>
<td>14.3</td>
<td>0.0</td>
<td>19.0</td>
</tr>
<tr>
<td>3.11 C₂H + H → C₂ + H₂</td>
<td>13.8</td>
<td>0.0</td>
<td>35.8</td>
</tr>
<tr>
<td>(II). C₁ and C₁ oxidation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.12 CH₄ + OH → CH₃ + H₂O</td>
<td>3.5</td>
<td>3.08</td>
<td>2.0</td>
</tr>
<tr>
<td>3.13 CH₄ + HO₂ → CH₃ + H₂O₂</td>
<td>13.3</td>
<td>0.0</td>
<td>18.0</td>
</tr>
<tr>
<td>3.14 CH₄ + O → CH₃ + OH</td>
<td>13.2</td>
<td>0.0</td>
<td>9.2</td>
</tr>
<tr>
<td>3.15 CH₃ + OH → CH₂O + H₂</td>
<td>12.6</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3.16 CH₃ + O → CH₂O + H</td>
<td>14.1</td>
<td>0.0</td>
<td>2.0</td>
</tr>
<tr>
<td>3.17 CH₂O + OH → HCO + H₂O</td>
<td>14.7</td>
<td>0.0</td>
<td>6.3</td>
</tr>
<tr>
<td>3.18 CH₂O + H → HCO + H₂</td>
<td>12.6</td>
<td>0.0</td>
<td>3.8</td>
</tr>
<tr>
<td>3.19 CH₂O + O → HCO + OH</td>
<td>13.7</td>
<td>0.0</td>
<td>4.6</td>
</tr>
<tr>
<td>3.20 HCO + OH → CO + H₂O</td>
<td>14.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Table A-1 (Continued)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>LogA (cm$^3$/mols)</th>
<th>n</th>
<th>$E_a$ (KJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.21 HCO + H → CO + H$_2$</td>
<td>14.3</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3.22 HCO + O → CO + OH</td>
<td>14.0</td>
<td>0.0</td>
<td>0.6</td>
</tr>
<tr>
<td>3.23 CO + OH → CO$_2$ + H</td>
<td>7.1</td>
<td>1.3</td>
<td>-0.8</td>
</tr>
<tr>
<td>3.24 CO + HO$_2$ → CO$_2$ + OH</td>
<td>14.0</td>
<td>0.0</td>
<td>23.0</td>
</tr>
<tr>
<td>3.25 CO$_2$ + O → CO + O$_2$</td>
<td>12.4</td>
<td>0.0</td>
<td>43.8</td>
</tr>
<tr>
<td>3.26 C$_2$H$_6$ + OH → C$_2$H$_5$ + H$_2$O</td>
<td>13.8</td>
<td>0.0</td>
<td>2.4</td>
</tr>
<tr>
<td>3.27 C$_2$H$_6$ + O → C$_2$H$_5$ + OH</td>
<td>13.4</td>
<td>0.0</td>
<td>6.4</td>
</tr>
<tr>
<td>3.28 C$_2$H$_5$ + O$_2$ → C$_2$H$_4$ + OH</td>
<td>12.0</td>
<td>0.0</td>
<td>5.0</td>
</tr>
<tr>
<td>3.29 C$_2$H$_4$ + O → CH$_3$ + HCO</td>
<td>13.0</td>
<td>0.0</td>
<td>1.1</td>
</tr>
<tr>
<td>3.30 C$_2$H$_4$ + OH → C$_2$H$_3$ + H$_2$O</td>
<td>14.0</td>
<td>0.0</td>
<td>3.5</td>
</tr>
<tr>
<td>3.31 C$_2$H$_3$ + O$_2$ → HCO + CH$_2$O</td>
<td>12.6</td>
<td>0.0</td>
<td>-1.05</td>
</tr>
<tr>
<td>3.32 C$_2$H$_2$ + O → C$_2$H + OH</td>
<td>13.8</td>
<td>0.0</td>
<td>4.0</td>
</tr>
<tr>
<td>3.33 C$_2$H + O → CO + CH</td>
<td>13.7</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3.34 CH$_2$ + O → CO + H$_2$</td>
<td>11.3</td>
<td>0.68</td>
<td>25.0</td>
</tr>
<tr>
<td>3.35 CH$_3$ + H → CH + H$_2$</td>
<td>11.4</td>
<td>0.67</td>
<td>25.7</td>
</tr>
<tr>
<td>3.36 CH + O → CO + H</td>
<td>13.8</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(III). Benzene pyrolysis and oxidation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.37 C$_6$H$_6$ → C$_6$H$_5$ + H</td>
<td>15.7</td>
<td>0.0</td>
<td>108.0</td>
</tr>
<tr>
<td>3.38 C$_6$H$_6$ + H → C$_6$H$_5$ + H$_2$</td>
<td>14.4</td>
<td>0.0</td>
<td>16.0</td>
</tr>
<tr>
<td>3.39 C$_6$H$_6$ + C$<em>6$H$<em>5$ → C$</em>{12}$H$</em>{10}$ + H</td>
<td>12.6</td>
<td>0.0</td>
<td>12.0</td>
</tr>
<tr>
<td>3.40 C$<em>{12}$H$</em>{10}$ → 2C$_6$H$_5$</td>
<td>14.9</td>
<td>0.0</td>
<td>103.0</td>
</tr>
<tr>
<td>3.41 C$_6$H$_5$ → C$_2$H$_2$ + C$_4$H$_3$</td>
<td>12.2</td>
<td>0.0</td>
<td>82.0</td>
</tr>
<tr>
<td>3.42 C$_6$H$_6$ → C$_2$H$_2$ + C$_4$H$_4$</td>
<td>14.1</td>
<td>0.0</td>
<td>76.0</td>
</tr>
<tr>
<td>3.43 C$_4$H$_3$ → C$_2$H + C$_2$H$_2$</td>
<td>14.3</td>
<td>0.0</td>
<td>57.0</td>
</tr>
</tbody>
</table>
The reverse reaction rate constants were calculated by the thermodynamic data or found from literature.

Table A-1 *(Continued)*

<table>
<thead>
<tr>
<th>Reaction</th>
<th>LogA (cm³/mols)</th>
<th>n</th>
<th>E_a (KJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.44 C₄H₄ → C₂H + C₂H₃</td>
<td>15.7</td>
<td>0.0</td>
<td>115.0</td>
</tr>
<tr>
<td>3.45 C₆H₆ + O₂ → C₆H₅ + HO₂</td>
<td>13.8</td>
<td>0.0</td>
<td>60.0</td>
</tr>
<tr>
<td>3.46 C₆H₆ + O → C₆H₅ + OH</td>
<td>14.5</td>
<td>0.0</td>
<td>6.0</td>
</tr>
<tr>
<td>3.47 C₆H₆ + OH → C₆H₅ + H₂O</td>
<td>13.3</td>
<td>0.0</td>
<td>4.5</td>
</tr>
<tr>
<td>3.48 C₆H₆ + HO₂ → C₆H₅ + H₂O₂</td>
<td>11.0</td>
<td>0.0</td>
<td>18.2</td>
</tr>
<tr>
<td>3.49 C₆H₅ + O₂ → 2CO + C₂H₂ + C₂H₃</td>
<td>12.0</td>
<td>0.0</td>
<td>1.9</td>
</tr>
</tbody>
</table>

(IV). O-H Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>LogA (cm³/mols)</th>
<th>n</th>
<th>E_a (KJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.50 H + O₂ → OH + O</td>
<td>14.3</td>
<td>0.0</td>
<td>16.8</td>
</tr>
<tr>
<td>3.51 H + H₂O → H₂ + OH</td>
<td>14.0</td>
<td>0.0</td>
<td>20.3</td>
</tr>
<tr>
<td>3.52 O + H₂ → H + OH</td>
<td>10.3</td>
<td>1.0</td>
<td>8.9</td>
</tr>
<tr>
<td>3.53 O + H₂O → 2OH</td>
<td>13.5</td>
<td>0.0</td>
<td>18.4</td>
</tr>
<tr>
<td>3.54 H₂ + Ar → 2H + Ar</td>
<td>12.4</td>
<td>-0.5</td>
<td>94.5</td>
</tr>
</tbody>
</table>

APPENDIX B. COMPUTER CODE

The computer code we used includes several functionality's. We will give the explanation here.

One major function we used in this model is subroutine **DIVPAG** (Double precision, solve an Initial-Value Problem for ordinary differential equations using and Adams-Moulton or Gear method, Gear method is used in our modeling). This saves much computer code. You will not find the coding for the ODE solving except a function call DIVPAG().

Following is the list of files:

- **model_main.f** main function includes read data, calculate initial concentration, call DIVPAG, determine the step size, test the tolerance, accumulate the reaction time.
- **initial.f** Calculate initial concentration of all components.
- **rate_const.f** Calculate the reaction rate of all chemicals in the reactor.
- **coag_const.f** Calculate the growth and coagulation rate of all particles.
- **yprime.f** Calculate the d[Conc]/dt, using by function FCN().
- **output.f** Output the results for the given reaction time.
- **redo_conc.f** Recalculate concentrations of all components after every step.
- **makefile** Compile and link all the functions
model_main.f

C MAIN PROGRAM: KINECTICS FOR MODELING CARBON BLACK
C PROCESS BY USING COAL AS FEEDSTOCK
C
C THIS VERSION LEAVES EVERYTHING IN PYROLYSIS AND
C OXIDATION
C********************************************************************************
C VARIABLE LIST
C********************************************************************************
C     Y(1)  =  C6H6  (BENZENE CONCENTRATION:  MOL/ML)
C     Y(2)  =  C6H5
C     Y(3)  =  C12H10
C     Y(4)  =  C4H4
C     Y(5)  =  C4H3
C     Y(6)  =  CH4
C     Y(7)  =  CH3
C     Y(8)  =  CH2
C     Y(9)  =  CH
C     Y(10) =  C2H6
C     Y(11) =  C2H5
C     Y(12) =  C2H4
C     Y(13) =  C2H3
C     Y(14) =  C2H2
C     Y(15) =  C2H
C     Y(16) =  C2
C     Y(17) =  H RADICAL
C     Y(18) =  O RADICAL
C     Y(19) =  OH
C     Y(20) =  H2
C     Y(21) =  H2O
C     Y(22) =  H2O2
C     Y(23) =  HO2
C     Y(24) =  O2
C     Y(25) =  CO
C     Y(26) =  CO2
C     Y(27) =  HCO
C     Y(28) =  CH2O
C     Y(29) =  ARGON
Y(30) = VOLATILE

Y(31-44) = PARTICLES

YP(1-44) = DERIVATIVES FOR CONCENTRATION CHANGE OF ALL REACTING SPECIES

All the gas-phase reactions considered in the model

\[ \begin{align*}
C6H6 & \rightarrow C6H5 + H \\
C6H6 + H & \rightarrow C6H5 + H2 \\
C6H6 + C6H5 & \rightarrow C12H10 + H \\
C12H10 & \rightarrow 2C6H5 \\
C6H5 & \rightarrow C2H2 + C4H3 \\
C6H6 & \rightarrow C2H2 + C4H4 \\
C4H3 & \rightarrow C2H + C2H2 \\
C4H4 & \rightarrow C2H + C2H3 \\
C6H6 + O2 & \rightarrow C6H5 + HO2 \\
C6H6 + O & \rightarrow C6H5 + OH \\
C6H6 + OH & \rightarrow C6H5 + H2O \\
C6H6 + HO2 & \rightarrow C6H5 + H2O2 \\
C6H5 + O2 & \rightarrow 2CO + C2H2 + C2H3 \\
CH4 & \rightarrow CH3 + H \\
CH4 + H & \rightarrow CH3 + H2 \\
C2H6 & \rightarrow CH3 + CH3 \\
C2H6 + CH3 & \rightarrow C2H5 + CH4 \\
C2H6 + H & \rightarrow C2H5 + H2 \\
C2H5 & \rightarrow C2H4 + H \\
C2H5 + CH3 & \rightarrow C2H4 + CH4 \\
C2H4 + H & \rightarrow C2H3 + H2 \\
C2H3 + M & \rightarrow C2H2 + H + M \\
C2H2 + H & \rightarrow C2H + H2 \\
C2H + H & \rightarrow C2 + H2 \\
CH4 + OH & \rightarrow CH3 + H2O \\
CH4 + HO2 & \rightarrow CH3 + H2O2 \\
CH4 + O & \rightarrow CH3 + OH \\
CH3 + OH & \rightarrow CH2O + H2 \\
CH3 + O & \rightarrow CH2O + H \\
CH2O + OH & \rightarrow HCO + H2O \\
CH2O + H & \rightarrow HCO + H2 \\
CH2O + O & \rightarrow HCO + OH
\end{align*} \]
C HCO + OH = CO + H2O (33)
C HCO + H = CO + H2 (34)
C HCO + O = CO + OH (35)
C CO + OH = CO2 + H (36)
C CO + HO2 = CO2 + OH (37)
C CO2 + O = CO + O2 (38)
C C2H6 + OH = C2H5 + H2O (39)
C C2H6 + O = C2H5 + OH (40)
C C2H5 + O2 = C2H4 + HO2 (41)
C C2H4 + O = CH3 + HCO (42)
C C2H4 + OH = C2H3 + H2O (43)
C C2H3 + O2 = HCO + CH2O (44)
C C2H2 + O = CH2 + CO (45)
C C2H + O = CO + CH (46)
C CH2 + O = CO + H2 (47)
C CH2 + H = CH + H2 (48)
C CH + O2 = HCO + O (49)
C
C H + O2 = OH + O (50)
C H + H2O = H2 + OH (51)
C O + H2 = H + OH (52)
C O + H2O = 2OH (53)
C H2 + M = 2H + M (54)
C
C COAL = VOLATILE + CHAR (55)

C === MAIN() FUNCTION --> beginning

PROGRAM MAIN
INTEGER NEQ, NPARAM, NRNEQ, NM, NP
PARAMETER (NEQ=44, NPARAM=50, NRNEQ=56, NM=28, NP=18)

INTEGER I, IDO, ISTEP, MXSTEP
REAL *8 PARAM(NPARAM), TINI, TEND, TMIN,
& TMAX, TOL, Y(NEQ)
INTRINSIC EXP, FLOAT, INT, MOD
EXTERNAL FCN, FCNJ, DINVAG, CTIME, STEPSIZE

INTEGER NFC(NRNEQ), NBC(NRNEQ), NMC(NM), NUC(NP)
REAL *8 FACT(NRNEQ), FTP(NRNEQ), FE(NRNEQ),
& BACT(NRNEQ), BTP(NRNEQ), BE(NRNEQ),
& AK(NM), BK(NM), CK(NM),
& PNU(NP),
& FC2H6, FCH4, FCO2, FCO, FH2,
& TEMP, TAR, GAS, WATER, VTOT

COMMON /A2/ NFC(NRNEQ), FACT(NRNEQ),
& FTP(NRNEQ), FE(NRNEQ)
COMMON /A3/ NBC(NRNEQ), BACT(NRNEQ),
& BTP(NRNEQ), BE(NRNEQ)
COMMON /A4/ NMC(NM), AK(NM), BK(NM), CK(NM)

COMMON /A6/ NUC(NP), PNU(NP)
COMMON /A7/ FC2H6, FCH4, FCO2, FCO, FH2
COMMON /A8/ TEMP, TAR, GAS, WATER, VTOT

INTEGER CODE
REAL *8 TOTAL_IN, TOTAL_C, TOTAL_H, TOTAL_O

C==== Initialize PARAM
  TEMP       = 1423.0
  MXSTEP     = 1E8
  TMAX       = 1.0

CALL SSET(NPARAM, 0.0, PARAM, 1)
PARAM(4) = MXSTEP
PARAM(12) = 2
PARAM(13) = 2
TOL       = 1.0E-6

C==== Initialize other arguments
  TINI       = 0.0
  TEND       = 0.0

DO 101 I = 1, NEQ
  Y(I) = 0.0
101

C==== Initialize volatile matter and its composition
WRITE(*,*) '1 for GASES as feedstock'
WRITE(*,*) '2 for OILS as feedstock'
WRITE(*,*) '3 for COAL as feedstock'

WRITE(6,*)
C  READ(5,*) CODE
CODE = 3

IF (CODE .EQ. 1) THEN
  CALL GINITIAL(NEQ,Y)
ELSEIF (CODE .EQ. 2) THEN
  CALL LINITIAL(NEQ,Y)
ELSEIF (CODE .EQ. 3) THEN
  CALL CINITIAL(NEQ,Y)
ELSE
  GOTO 1000
ENDIF

C==== To check C, H, or O balance
C==== initial carbon
TOTAL_C = 6.0*(Y(1)+Y(2)) + 12.0*Y(3) + 4.0*(Y(4)+Y(5))
& + (Y(6)+Y(7)+Y(8)+Y(9)+Y(25)+Y(26)+Y(27)+Y(28))
& + 2.0*(Y(10)+Y(11)+Y(12)+Y(13)+Y(14)+Y(15)+Y(16))

C==== initial hydrogen
TOTAL_H = 6.0*(Y(1)+Y(10)) + 5.0*(Y(2)+Y(11)) + 10.0*Y(3)
& + 4.0*(Y(4)+Y(6)+Y(12)) + 3.0*(Y(5)+Y(7)+Y(13)) + Y(9)
& + 2.0*(Y(8)+Y(14)+Y(20)+Y(21)+Y(22)+Y(28))
& + Y(9)+Y(15)+Y(17)+Y(19)+Y(23)+Y(27)

C==== initial oxygen
TOTAL_O = Y(18)+Y(19)+Y(21)+Y(25)+Y(27)+Y(28)
& + 2.0*(Y(22)+Y(23)+Y(24)+Y(26))

C TOTAL_IN = TOTAL_C
C TOTAL_IN = TOTAL_H
TOTAL_IN = TOTAL_O

C==== Read data form data files
OPEN (UNIT=2, FILE='forward.dat')
OPEN (UNIT=3, FILE='backward.dat')
OPEN (UNIT=4, FILE='particle.dat')
  read(2,*) (NPC(I),FACT(I),FTP(I),FE(I),I=1,NRNEQ-1)
  read(3,*) (NBC(I),BACT(I),BTP(I),BE(I),I=1,24)
  read(3,*) (NMC(I),AK(I),BK(I),CK(I),I=1,NM)
  read(4,*) (NUC(I),PNU(I),I=1,NP)
CLOSE(2)
CLOSE(3)
CLOSE(4)
C==== Integrate ODE system
OPEN (UNIT=11, FILE='data/fort.11')
OPEN (UNIT=12, FILE='data/fort.12')
OPEN (UNIT=21, FILE='data/fort.21')
OPEN (UNIT=22, FILE='data/fort.22')
OPEN (UNIT=23, FILE='data/fort.23')
OPEN (UNIT=24, FILE='data/fort.24')
OPEN (UNIT=25, FILE='data/fort.25')
OPEN (UNIT=51, FILE='data/fort.51')
OPEN (UNIT=52, FILE='data/fort.52')
OPEN (UNIT=53, FILE='data/fort.53')
OPEN (UNIT=54, FILE='data/fort.54')
OPEN (UNIT=55, FILE='data/fort.55')
OPEN (UNIT=56, FILE='data/fort.56')
OPEN (UNIT=57, FILE='data/fort.57')
OPEN (UNIT=58, FILE='data/fort.58')
OPEN (UNIT=59, FILE='data/fort.59')

IDO = 1
ISTEP = 0
LL = 10
TMIN = TMAX/FLOAT(MXSTEP)

DO 150 WHILE (TEND .LT. TMAX)
   ISTEP = ISTEP + 1
   CALL STEPSIZE(ISTEP, LL, TEND, TMIN)
   CALL HEAT_BALANCE (NEQ, NRN, TEMP, TEND, Y)
   TEND = TINI+TMIN
   CALL DIVPAG(IDO, NEQ, FCN, FCNJ, A, TINI, TEND, TOL, PARAM, Y)
   WRITE(*,*) ISTEP
   CALL OUTPUT (NEQ, NRNEQ, ISTEP, PNU, TOTAL_IN, Y, TEND)
150 CONTINUE

CALL OUTPUT (NEQ, NRNEQ, ISTEP, PNU, TOTAL_IN, Y, TEND)

C==== Final call to resease workspace
CALL DIVPAG(3, NEQ, FCN, FCNJ, A, TINI, TEND, TOL, PARAM, Y)

CLOSE(11)
CLOSE(12)
CLOSE(21)
CLOSE (22)
CLOSE (23)
CLOSE (24)
CLOSE (25)
CLOSE (51)
CLOSE (52)
CLOSE (53)
CLOSE (54)
CLOSE (55)
CLOSE (56)
CLOSE (57)
CLOSE (58)
CLOSE (59)

1000 STOP
END
C==== end of MAIN() function

C==== SUBROUTINE BELOW ====
C==== subroutine FCN()  
SUBROUTINE FCN (FCNNEQ, XI, Y, YP)
  INTEGER FCNNEQ
  REAL *8 XI, Y (FCNNEQ), YP (FCNNEQ)
  PARAMETER (NRN=55, NPN=18)
  REAL *8 RATE (NRN), RAD (NPN), FXY (NPN, NPN),
           QXY (NPN, NPN)
  INTEGER NUC (NPN)
  REAL *8 PNU (NP), TEMP, TAR, GAS, WATER, VTOT
  COMMON /A6/ NUC (NPN), PNU (NPN)
  COMMON /A8/ TEMP, TAR, GAS, WATER, VTOT
  EXTERNAL HEAT_BALANCE, RATE_CONST, COAG_CONST, YPRIME
  CALL COAG_CONST (NPN, RAD, PNU, FXY, QXY, TEMP)
  CALL RATE_CONST (FCNNEQ, NRN, TEMP, Y, RATE)
  CALL YPRIME (FCNNEQ, NRN, NPN, RATE, FXY, QXY, PNU, Y, YP)
  RETURN
END
C==== end of FCN()
C==== subroutine FCNJ()
SUBROUTINE FCNJ(N,X,Y,PD)
INTEGER N
REAL *8 X,Y(N),PD(N,N)
RETURN
END
C==== end of FCNJ()

C==== subroutine STEPSIZE()
SUBROUTINE STEPSIZE(ISTEP,LL,TEND,TMIN)
INTEGER ISTEP,LL
REAL *8 TEND,TMIN

C==== the step size is increased with the increasing of the loop
IF (ISTEP .LT. 2**(LL+4)) THEN
  TEND = TEND + TMIN
ELSE IF (ISTEP .LT. 2**(LL+5)) THEN
  TEND = TEND + (2**1)*TMIN
ELSE IF (ISTEP .LT. 2**(LL+6)) THEN
  TEND = TEND + (2**2)*TMIN
ELSE IF (ISTEP .LT. 2**(LL+7)) THEN
  TEND = TEND + (2**3)*TMIN
ELSE IF (ISTEP .LT. 2**(LL+8)) THEN
  TEND = TEND + (2**4)*TMIN
ELSE IF (ISTEP .LT. 2**(LL+9)) THEN
  TEND = TEND + (2**5)*TMIN
ELSE IF (ISTEP .LT. 2**(LL+10)) THEN
  TEND = TEND + (2**6)*TMIN
ELSE IF (ISTEP .LT. 2**(LL+11)) THEN
  TEND = TEND + (2**8)*TMIN
ELSE IF (ISTEP .LT. 2**(LL+12)) THEN
  TEND = TEND + (2**10)*TMIN
ELSE
  TEND = TEND + (2**12)*TMIN
ENDIF
RETURN
END
C==== end of subroutine stepsize()
C==== CINITIAL() function is used to calculate the
C==== initial conditions for all the possible species WITH
C==== COAL feedstock

SUBROUTINE CINITIAL(COALNEQ,Y)
INTEGER COALNEQ
REAL *8 Y(COALNEQ)
PARAMETER (INI_NEQ=56,INI_GAS=28,INI_PAT=18)
CHARACTER CHAR
REAL *8 R,P,ROOMT,REACT,V,RCOAL,RO2,RH2O,RCO,RN2
REAL *8 TCONC,VOLAT,CTOTAL,TVOLAT,PRE_VOLAT,FRAC
REAL *8 MC6H6, MH2O, MCO2, MCO, MH2, MCH4, MC2H6
INTEGER NFC(INI_NEQ),NBC(INI_NEQ),NMC(INI_GAS),
& NUC(INI_PAT)
REAL *8 FACT(INI_NEQ),FTP(INI_NEQ),FE(INI_NEQ),
& BACT(INI_NEQ),BTP(INI_NEQ),BE(INI_NEQ),
& AK(INI_GAS),BK(INI_GAS),CK(INI_GAS),
& PNU(INI_PAT),
& FC2H6, FCH4, FCO2, FCO, FH2,
& TEMP, TAR, GAS, WATER, VTOT

COMMON /A2/ NFC(INI_NEQ),FACT(INI_NEQ),FTP(INI_NEQ),
& FE(INI_NEQ)
COMMON /A3/ NBC(INI_NEQ),BACT(INI_NEQ),BTP(INI_NEQ),
& BE(INI_NEQ)
COMMON /A4/ NMC(INI_GAS),AK(INI_GAS),BK(INI_GAS),
& CK(INI_GAS)
COMMON /A6/ NUC(INI_PAT),PNU(INI_PAT)
COMMON /A7/ FC2H6, FCH4, FCO2, FCO, FH2
COMMON /A8/ TEMP, TAR, GAS, WATER, VTOT

C==== Read data form data files
OPEN (UNIT=2, FILE='forward.dat')
OPEN (UNIT=3, FILE='backward.dat')
OPEN (UNIT=4, FILE='particle.dat')
read(2,*)(NFC(I),FACT(I),FTP(I),FE(I),I=1,INI_NEQ-1)
read(3,*)(NBC(I),BACT(I),BTP(I),BE(I),I=1,24)
read(3,*)(NMC(I),AK(I),BK(I),CK(I),I=1,INI_GAS)
read(4,*)(NUC(I),PNU(I),I=1,INI_PAT)
CLOSE(2)
CLOSE(3)
CLOSE(4)

C ==== initialize the composition of gases
FC2H6 = 0.065
FCH4 = 0.625
FCO2 = 0.105
FCO = 0.145
FH2 = 0.060

C ==== initialize the tar composition and the gas concentration
OPEN (UNIT=3, FILE='cinitial.dat')
READ(3,*), CHAR, ROOMT
READ(3,*), CHAR, REACT
READ(3,*), CHAR, V
READ(3,*), CHAR, TAR, GAS, WATER
READ(3,*), CHAR
READ(3,*), CHAR, RCOAL
READ(3,*), CHAR, RO2
READ(3,*), CHAR, RCO
READ(3,*), CHAR, RH2O
READ(3,*), CHAR, RN2
CLOSE(3)

C==== calculate the initial concentration
R = 82.06
P = 1.0
FRAC = 1.0
ROOMT = ROOMT+273.0
REACT = REACT+273.0
TEMP = REACT

C translate all feed gases into ml/sec at reaction temperature
RH2O = RH2O/18.0/60.0
RO2 = RO2/22.4/60.0
RCO = RCO/22.4/60.0
RN2 = RN2/22.4/60.0

C translate coal feed rate into volatile in unit of g/sec.ml
VOLAT = ((1.0-FRAC)*RCOAL*V)*(1000.0/3600.0)
PRE_VOLAT = FRAC*RCOAL*V*(1000.0/3600.0)
MC6H6 = PRE_VOLAT*TAR/78.0
MH2O = PRE_VOLAT*WATER/18.0
MCO2 = (PRE_VOLAT*GAS*FCO2)/44.0
MCO = (PRE_VOLAT*GAS*FCO)/28.0
MH2 = (PRE_VOLAT*GAS*FH2)/2.0
MCH4 = (PRE_VOLAT*GAS*FCH4)/16.0
MC2H6 = (PRE_VOLAT*GAS*FC2H6)/30.0

TVOLAT = MC6H6+MH2O+MCO2+MCO+MH2+MCH4+MC2H6
CTOTAL = RO2+RCO+RN2+RH2O+TVOLAT
TCONC = P/(R*REACT)

Y (1) = MC6H6*TCONC/CTOTAL
Y (6) = MCH4*TCONC/CTOTAL
Y (10) = MC2H6*TCONC/CTOTAL
Y (20) = MH2*TCONC/CTOTAL
Y (21) = (MH2O+RH2O)*TCONC/CTOTAL
Y (24) = RO2*TCONC/CTOTAL
Y (25) = (MCO+RCO)*TCONC/CTOTAL
Y (26) = MCO2*TCONC/CTOTAL
Y (29) = RN2*TCONC/CTOTAL/80.0
Y (30) = VOLAT

RETURN
END

C==== end of COAL_INITIAL()

C==== GINITIAL() function is used to define the initial
C==== condition for all the possible species WITH GASes
C==== feedstock.

SUBROUTINE GINITIAL(NEQ,Y)
INTEGER NEQ
REAL *8 Y(NEQ)
REAL *8 CAr,CH2,CCH4
REAL *8 TEMP,TAR,GAS,WATER,VTOT
COMMON /A8/ TEMP,TAR,GAS,WATER,VTOT

TEMP = 1523
CAr = 2.6D20
CCH4 = 6.0D19
CH2 = 2.5D19
RETURN
END
C==== end of GAS-INITIAL()

C==== LIQUID-INITIAL() function is used to calculate the initial conditions for all the possible species WITH AROMATICS feedstock

SUBROUTINE LIQUID-INITIAL(NEQ, Y)
INTEGER NEQ
REAL *8 Y(NEQ)
REAL *8 TEMP

TEMP = 1800
CC6H6 = 3.05D-04
CO2 = 4.15D-04
c CH2O = 7.86D-04
c CCO2 = 5.00D-04
N2 = 4.64D-03
CAr = N2/20.0

c Y(1) = CC6H6/1000.0
Y(21) = CH2O/1000.0
Y(24) = CO2/1000.0
c Y(26) = CCO2/1000.0
Y(29) = CAr/1000.0

RETURN
END
C==== end of LIQUID-INITIAL()
rate_const.f

C==== RATE_CONST() is used to calculate the gas reaction rates

SUBROUTINE RATE_CONST(NEQ,NR,TEMP,Y,RATE)
INTEGER NEQ,NR
REAL *8 TEMP,Y(NEQ),RATE(NR)
REAL *8 FWK(55),BWK(55),AVOG

AVOG = 6.023D23

C==== calculate the rate constants
CALL BENZENE(NR,FWK,BWK,TEMP,AVOG)
CALL METHANE(NR,FWK,BWK,TEMP,AVOG)

C==== calculate the reaction rate
C==== benzene pyrolysis
RATE(1) = FWK(1)*Y(1) - BWK(1)*Y(2)*Y(17)
RATE(2) = FWK(2)*Y(1)*Y(17) - BWK(2)*Y(2)*Y(20)
RATE(3) = FWK(3)*Y(1)*Y(2) - BWK(3)*Y(3)*Y(17)
RATE(4) = FWK(4)*Y(3) - BWK(4)*Y(2)**2
RATE(5) = FWK(5)*Y(2) - BWK(5)*Y(5)*Y(14)
RATE(6) = FWK(6)*Y(1) - BWK(6)*Y(4)*Y(14)
RATE(7) = FWK(7)*Y(5) - BWK(7)*Y(14)*Y(15)
RATE(8) = FWK(8)*Y(4) - BWK(8)*Y(13)*Y(15)

C==== benzene oxidations
RATE(9) = FWK(9)*Y(1)*Y(24) - BWK(9)*Y(2)*Y(23)
RATE(10) = FWK(10)*Y(1)*Y(18) - BWK(10)*Y(2)*Y(19)
RATE(11) = FWK(11)*Y(1)*Y(19) - BWK(11)*Y(2)*Y(21)
RATE(12) = FWK(12)*Y(1)*Y(23) - BWK(12)*Y(2)*Y(22)
RATE(13) = FWK(13)*Y(2)*Y(24) -
& BWK(13)*Y(14)*Y(13)*Y(25)**2

C==== methane pyrolysis
RATE(14) = FWK(14)*Y(6) - BWK(14)*Y(7)*Y(17)
RATE(15) = FWK(15)*Y(6)*Y(17) - BWK(15)*Y(7)*Y(20)
RATE(16) = FWK(16)*Y(10) - BWK(16)*Y(7)**2
RATE(17) = FWK(17)*Y(10)*Y(7) - BWK(17)*Y(11)*Y(6)
RATE(18) = FWK(18)*Y(10)*Y(17) - BWK(18)*Y(11)*Y(20)
RATE(19) = FWK(19)*Y(11) - BWK(19)*Y(12)*Y(17)
RATE(20) = FWK(20)*Y(11)*Y(7) - BWK(20)*Y(12)*Y(6)
RATE(21) = FWK(21) * Y(12) * Y(17) - BWK(21) * Y(13) * Y(20)
RATE(22) = FWK(22) * Y(13) * Y(29) -
& BWK(22) * Y(14) * Y(17) * Y(29)
RATE(23) = FWK(23) * Y(14) * Y(17) - BWK(23) * Y(15) * Y(20)
RATE(24) = FWK(24) * Y(15) * Y(17) - BWK(24) * Y(16) * Y(20)

C==== C1 oxidations
RATE(26) = FWK(26) * Y(6) * Y(23) - BWK(26) * Y(7) * Y(22)
RATE(27) = FWK(27) * Y(6) * Y(18) - BWK(27) * Y(7) * Y(19)
RATE(28) = FWK(28) * Y(7) * Y(19) - BWK(28) * Y(28) * Y(20)
RATE(29) = FWK(29) * Y(7) * Y(18) - BWK(29) * Y(28) * Y(17)
RATE(30) = FWK(30) * Y(28) * Y(19) - BWK(30) * Y(27) * Y(21)
RATE(31) = FWK(31) * Y(28) * Y(17) - BWK(31) * Y(27) * Y(20)
RATE(32) = FWK(32) * Y(28) * Y(18) - BWK(32) * Y(27) * Y(19)
RATE(33) = FWK(33) * Y(27) * Y(19) - BWK(33) * Y(25) * Y(21)
RATE(34) = FWK(34) * Y(27) * Y(17) - BWK(34) * Y(25) * Y(20)
RATE(35) = FWK(35) * Y(27) * Y(18) - BWK(35) * Y(25) * Y(19)
RATE(36) = FWK(36) * Y(25) * Y(19) - BWK(36) * Y(26) * Y(17)
RATE(37) = FWK(37) * Y(25) * Y(23) - BWK(37) * Y(26) * Y(19)
RATE(38) = FWK(38) * Y(26) * Y(18) - BWK(38) * Y(25) * Y(24)

C==== C2 oxidations
RATE(39) = FWK(39) * Y(10) * Y(19) - BWK(39) * Y(11) * Y(21)
RATE(40) = FWK(40) * Y(10) * Y(18) - BWK(40) * Y(11) * Y(19)
RATE(41) = FWK(41) * Y(11) * Y(24) - BWK(41) * Y(12) * Y(23)
RATE(42) = FWK(42) * Y(12) * Y(18) - BWK(42) * Y(7) * Y(27)
RATE(43) = FWK(43) * Y(12) * Y(19) - BWK(43) * Y(13) * Y(21)
RATE(44) = FWK(44) * Y(13) * Y(24) - BWK(44) * Y(27) * Y(28)
RATE(45) = FWK(45) * Y(14) * Y(18) - BWK(45) * Y(8) * Y(25)
RATE(46) = FWK(46) * Y(15) * Y(18) - BWK(46) * Y(9) * Y(25)
RATE(47) = FWK(47) * Y(8) * Y(18) - BWK(47) * Y(25) * Y(20)
RATE(48) = FWK(48) * Y(8) * Y(17) - BWK(48) * Y(9) * Y(20)
RATE(49) = FWK(49) * Y(9) * Y(24) - BWK(49) * Y(27) * Y(18)

C==== O-H balance
RATE(50) = FWK(50) * Y(17) * Y(24) - BWK(50) * Y(18) * Y(19)
RATE(51) = FWK(51) * Y(17) * Y(21) - BWK(51) * Y(20) * Y(19)
RATE(52) = FWK(52) * Y(18) * Y(20) - BWK(52) * Y(17) * Y(19)
RATE(53) = FWK(53) * Y(18) * Y(21) - BWK(53) * Y(19) **2
RATE(54) = FWK(54) * Y(20) * Y(29) -
& BWK(54) * (Y(17) **2) * Y(29)

C==== COAL pyrolysis
RATE(55) = FWK(55)*(Y(30))

RETURN
END
C==== end of rate_const() function

C==== rate constant calculation BENZENE()
C==== Variables explanation
C
C ACT   constant
C PT    constant
C E     activity energy, kcal/mole
C FWK(NEQ) forward rate constant of reaction I
C FWK(I) = ACT(I)*TEMP^PT(I)*EXP(-E(I)/(R*TEMP))
C BACT  constant
C BPT   constant
C BE    activity energy, kcal/mole
C BWK(NEQ) backward rate constant of reaction I
C BWK(I) = BACT(I)*TEMP^BPT(I)*EXP(-BE(I)/(R*TEMP))

SUBROUTINE BENZENE(NR, FWK, BWK, TEMP, AVOG)
INTEGER NR
REAL *8 FWK(NR), BWK(NR), TEMP, AVOG

PARAMETER (MEQ = 56)
INTEGER NFC(MEQ), NBC(MEQ)
REAL *8 FACT(MEQ), FTP(MEQ), FE(MEQ),
& BACT(MEQ), BTP(MEQ), BE(MEQ)
COMMON /A2/ NFC(MEQ), FACT(MEQ), FTP(MEQ), FE(MEQ)
COMMON /A3/ NBC(MEQ), BACT(MEQ), BTP(MEQ), BE(MEQ)
REAL *8 TMP_FA, TMP_FP, TMP_FE, TMP_BA, TMP_BP, TMP_BE

DO 320 I=1,13
   TMP_FA = 10**FACT(I)
   TMP_FP = TEMP**FTP(I)
   TMP_FE = 1000.*FE(I)/(1.987*TEMP)
   FWK(I) = TMP_FA*TMP_FP*EXP(-TMP_FE)

   IF (BACT(I) .eq. 0.0) goto 321

   TMP_BA = 10**BACT(I)

320 CONTINUE
TMP_BP = TEMP**BTP(I)
TMP_BE = 1000.*BE(I)/(1.987*TEMP)
BWK(I) = TMP_BA*TMP_BP*EXP(-TMP_BE)
goto 320
321 BWK(I) = 0.0
320 CONTINUE

RETURN
END
C==== end of BENZENE() ====

C==== rate constant calculation METHANE() ====
C==== Variables explanation
C
C AK,BK,CK   constants
C K(NN)   equilibrium constant of matter I
C log(K) = (AK(I) + BK(I)*TEMP + CK(I)*TEMP**2)
C EK(NN)   equilibrium constant of reaction I
C log(EK(I)) = sum of log(Kf).
C
SUBROUTINE METHANE(NR,FWK,BWK,TEMP,AVOG)
INTEGER NR
REAL*8 FWK(NR),BWK(NR),TEMP,AVOG

PARAMETER (MEQ=56,MN=28)

INTEGER NFC(MEQ),NBC(MEQ),NMC(MN)
REAL*8 FACT(MEQ),FTP(MEQ),FE(MEQ),
& BACT(MEQ),BTP(MEQ),BE(MEQ),
& AK(MN),BK(MN),CK(MN)
COMMON /A2/ NFC(MEQ),FACT(MEQ),FTP(MEQ),FE(MEQ)
COMMON /A3/ NBC(MEQ),BACT(MEQ),BTP(MEQ),BE(MEQ)
COMMON /A4/ NMC(MN),AK(MN),BK(MN),CK(MN)

REAL*8 K(MEQ),EK(MEQ),TMP_FA,TMP_FP,TMP_FE

INTRINSIC EXP,LOG

DO 330 I=1,MN
   K(I) = 10**(AK(I) + BK(I)*TEMP + CK(I)*TEMP**2)
330 CONTINUE
C==== pyrolysis equilibrium constants
EK(14) = K(7) * K(17) / (K(6))
EK(15) = K(7) / (K(6) * K(17))
EK(16) = K(7) * 2 / (K(10))
EK(17) = K(6) * K(11) / (K(7) * K(10))
EK(18) = K(11) / (K(10) * K(17))

EK(20) = K(12) * K(6) / (K(11) * K(7))
EK(21) = K(13) / (K(12) * K(17))
EK(22) = K(14) / (K(13) * K(17))
EK(23) = K(15) / (K(14) * K(17))
EK(24) = K(16) / (K(15) * K(17))

C==== C1 oxidation
EK(25) = K(7) * K(21) / (K(6) * K(19))
EK(26) = K(7) * K(22) / (K(6) * K(23))
EK(27) = K(7) * K(19) / (K(6) * K(18))
EK(28) = K(28) / (K(7) * K(19))
EK(29) = K(28) * K(17) / (K(7) * K(18))

EK(30) = K(27) * K(21) / (K(28) * K(19))
EK(31) = K(27) / (K(28) * K(17))
EK(32) = K(27) * K(19) / (K(28) * K(18))
EK(33) = K(25) * K(21) / (K(27) * K(19))
EK(34) = K(25) / (K(27) * K(17))
EK(35) = K(25) * K(19) / (K(27) * K(18))

EK(36) = K(26) * K(17) / (K(25) * K(19))
EK(37) = K(26) * K(19) / (K(25) * K(23))
EK(38) = K(25) / (K(26) * K(18))

C==== C2 oxidation
EK(39) = K(11) * K(21) / (K(10) * K(19))
EK(40) = K(11) * K(19) / (K(10) * K(18))
EK(41) = K(12) * K(23) / (K(11))
EK(42) = K(7) * K(27) / (K(12) * K(18))
EK(43) = K(13) * K(21) / (K(12) * K(19))

EK(44) = K(27) * K(28) / (K(13))
EK(45) = K(8) * K(25) / (K(14) * K(18))
EK(46) = K(9) * K(25) / (K(15) * K(18))
EK(47) = K(25) / (K(8) * K(18))
EK(48) = K(9) / (K(8) * K(17))
EK(49) = K(27) * K(18) / (K(9) * K(24))
C==== O-H balance
EK(50) = K(18)*K(19)/(K(17))
EK(51) = K(19)/(K(17)*K(21))
EK(52) = K(17)*K(19)/(K(18))
EK(53) = K(19)**2/(K(18)*K(21))
EK(54) = K(17)**2

C==== Calculate forward rate constants for reactions
C==== from 14 to 54
DO 332 I=14,MEQ-1
    TMP_FAc = 10**FACT(I)
    TMP_FP = TEMP**FTP(I)
    TMP_FE = 1000.*FE(I)/(1.987*TEMP)
    FWK(I) = TMP_FAc*TMP_FP*EXP(-TMP_FE)
332 CONTINUE

C==== Calculate backward rate constants for reactions
C==== from 14 to 24
DO 334 I=14,24
    TMP_BA = 10**BACT(I)
    TMP_BP = TEMP**BTP(I)
    TMP_BE = 1000.*BE(I)/(1.987*TEMP)
    BWK(I) = TMP_BA*TMP_BP*EXP(-TMP_BE)
334 CONTINUE
    BWK(17) = FWK(17)/EK(17)
    BWK(20) = FWK(20)/EK(20)

C==== Calculate backward rate constants for all other
C==== reactions by using each individual equilibrium
C==== constants
DO 336 I=25,MEQ-2
    BWK(I) = FWK(I)/EK(I)
336 CONTINUE
    BWK(54) = (10**(11.74))*
             (TEMP**(-0.5))*EXP(11900/(1.987*TEMP))
    BWK(55) = 0.0

RETURN
END
C==== end of METHANE() ====
C===== COAG_CONST() function is used to calculate the
C===== coagulation constants between particles

SUBROUTINE COAG_CONST(NP,RI,PNU,FXY,QXY,TEMP)
INTEGER NP
REAL *8 RI(NP),FXY(NP,NP),QXY(NP,NP),PNU(NP),TEMP
REAL *8 PI,AVOG,BOLTZ

PI   = 3.14159
AVOG = 6.023D23
BOLTZ = 1.3807D-16

C===== radius calculation for each particle class
DO 210 I=1,NP
   RI(I) = (0.75*PNU(I)*(12./AVOG)/(2.0*PI))**0.3333
210 CONTINUE

C===== Calculate FXY(I,J), Three different mechanisms
C===== were checked.
c CALL FUCH(NP,RI,FXY,PI,AVOG,TEMP)
c CALL JENSEN(NP,RI,FXY,BOLTZ,AVOG,TEMP)
c CALL IVIE(NP,RI,PNU,FXY,PI,BOLTZ,AVOG,TEMP)

C===== Calculate QXY(I,J)
DO 215 I=1,NP-2
   QXY(I,I) = FXY(I,I)*PNU(I)/PNU(I+1)
DO 216 J=1,NP-2
   IF (J .LE. I) goto 216
   QXY(I,J) = FXY(I,J)*PNU(I)/(PNU(J+1)-PNU(J))
216 CONTINUE
215 CONTINUE

RETURN
END
C===== end of COAG_CONST()
C==== Fuch's formula for coagulation rate calculation
C==== FXY(I,J)

SUBROUTINE FUCH(NP,RI,FXY,PI,AVOG,TEMP)
INTEGER NP
REAL *8 RI(NP),FXY(NP,NP), PI,AVOG,TEMP
REAL *8 D(20),G(20),L(20),DELT(20),RXY,DXY,GXY
REAL *8 C1,C2,DELTXY,COMB
INTRINSIC EXP,LOG,SQRT

DO 220 I=1,NP
   C1 = LOG(RI(I))
   D(I) = EXP(-30.37 - 1.566*C1)
   G(I) = EXP(-15.6697 - 1.5002*C1)
   L(I) = 8*D(I)/(PI*G(I))
   C2 = (2*RI(I)+L(I))**3 -(4*RI(I)**2+L(I)**2)**(1.5)
   DELT(I) = SQRT(2.0)*(C2/(6*RI(I)*L(I)) - 2*RI(I))
220 CONTINUE

DO 225 I=1,NP
   DO 226 J=1,NP
      DXY = D(I) + D(J)
      RXY = RI(I) + RI(J)
      GXY = SQRT(G(I)**2+G(J)**2)
      DELTXY = SQRT(DELT(I)**2+DELT(J)**2)
      COMB = 1/(1+DELTXY/RXY) + 4*DXY/GXY/RXY
      FXY(I,J) = (2*PI*DXY*RXY/COMB)
      FXY(I,J) = FXY(I,J)*AVOG
226 CONTINUE
225 CONTINUE

RETURN
END
C==== end of subroutine function FUCH()
C==== Jensen's formula for coagulation rate calculation
C==== FXY(I,J)

SUBROUTINE JENSEN(NP, RI, FXY, BOLTZ, AVOG, TEMP)
INTEGER NP
REAL *8 RI(NP), FXY(NP,NP), BOLTZ, AVOG, TEMP
REAL *8 C3, C4, VOL
INTRINSIC SQRT

VOL = 12.0/AVOG/2.0

DO 235 I=1,NP
   DO 236 J=1,NP
      C4 = (RI(I)+RI(J))**4.0
      C3 = 1/(RI(I)**3.0) + 1/(RI(J)**3.0)
      FXY(I,J) = SQRT(VOL*TEMP*BOLTZ*AVOG*C3*C4/2.)
      FXY(I,J) = FXY(I,J)*AVOG
   236 CONTINUE
235 CONTINUE

RETURN
END
C==== end of subroutine function JENSEN()

C==== Ivie's formula for coagulation rate calculation
C==== FXY(I,J)

SUBROUTINE IVIE(NP, RI, PNU, FXY, PI, BOLTZ, AVOG, TEMP)
INTEGER NP
REAL *8 RI(NP), PNU(NP), FXY(NP,NP),
&       PI, BOLTZ, AVOG, TEMP
REAL *8 PRES, C1, CON, VIS, RA, W, SLAM, U1, U2,
&       B1, B2, D1, D2, F
INTRINSIC EXP, LOG, SQRT

PRES  = 1.0
CON   = 12.0/AVOG
C1    = 1.81D-04*(1.0/293.**0.5)*(1.+111.3/293.)
VIS   = C1*TEMP**1.5/(TEMP+111.3)
DO 245 I=1,NP
DO 246 J=1,NP

RA = PI*(RI(I)+RI(J))*2
W = PNU(I)*PNU(J)*CON/(PNU(I)+PNU(J))

SLAM = 2.18D-08*TEMP/PRES
U1 = SLAM/RI(I)
U2 = SLAM/RI(J)
B1 = (1.+0.864*U1+0.29*U1*EXP(-1.25/U1))/
& (6.*PI*VIS*RI(I))
B2 = (1.+0.864*U2+0.29*U2*EXP(-1.25/U2))/
& (6.*PI*VIS*RI(J))
D1 = BOLTZ*TEMP*B1
D2 = BOLTZ*TEMP*B2
f = 4.*(D1+D2)/(RI(I)+RI(J))*
& (W*PI/(8.*BOLTZ*TEMP))**0.5

FXY(I,J) = 2.*PI*(RI(I)+RI(J))*(B1+B2)*BOLTZ*TEMP*
& (1./(1.+f))
FXY(I,J) = FXY(I,J)*AVOG

246 CONTINUE
245 CONTINUE

RETURN
END
C==== end of subroutine function IVIE()
yprime.f

C==== YPRIME() function was used to calculate dy/dt
C==== (YP, in the code), and return dy/dt to FCN() function

SUBROUTINE YPRIME (NEQ, NRNEQ, NPN, R, FXY, QXY, PNU, Y, YP)
INTEGER NEQ, NRNEQ, NPN
REAL *8 R (NRNEQ), FXY (NPN, NPN), QXY (NPN, NPN),
& PNU (NPN), Y (NEQ), YP (NEQ)
REAL *8 GROW2, GROW4, GROWTH2, GROWTH4, O_SHRINK
REAL *8 A(20), B(20), C(20), D(20)
REAL *8 C6H6, H2O, C2H6, CH4, CO2, CO, H2, FC2H6, FCH4
REAL *8 FCO2, FCO, FH2, TEMP, TAR, GAS, WATER, VTOT

COMMON /A7/ FC2H6, FCH4, FCO2, FCO, FH2
COMMON /A8/ TEMP, TAR, GAS, WATER, VTOT

C==== get the portion from pyrolysis of coal
C6H6 = R(55)*TAR/78.0
H2O = R(55)*WATER/18.0
C2H6 = R(55)*GAS*FC2H6/30.0
CH4 = R(55)*GAS*FCH4/16.0
CO2 = R(55)*GAS*FCO2/44.0
CO = R(55)*GAS*FCO/28.0
H2 = R(55)*GAS*FH2/2.0

C==== growth species C2 and C4
GROW2 = Y(13)+Y(14)+Y(15)+Y(16)
GROW4 = Y(4)+Y(5)

C==== growth reactions
GROWTH2 = FXY(1,2)*Y(31) + FXY(1,5)*Y(32)
& +FXY(1,6)*Y(33) + FXY(1,7)*Y(34)
& +FXY(1,8)*Y(35) + FXY(1,9)*Y(36)
& +FXY(1,10)*Y(37) + FXY(1,11)*Y(38)
& +FXY(1,12)*Y(39) + FXY(1,13)*Y(40)
& +FXY(1,14)*Y(41) + FXY(1,15)*Y(42)
& +FXY(1,16)*Y(43)

GROWTH4 = FXY(2,2)*Y(31) + FXY(2,5)*Y(32)
& +FXY(2,6)*Y(33) + FXY(2,7)*Y(34)
& +FXY(2,8)*Y(35) + FXY(2,9)*Y(36)
& +FXY(2,10)*Y(37) + FXY(2,11)*Y(38)
\& +FXY(2,12) \ast Y(39) + FXY(2,13) \ast Y(40) \\
\& +FXY(2,14) \ast Y(41) + FXY(2,15) \ast Y(42) \\
\& +FXY(2,16) \ast Y(43) \\

\textbf{c==== oxidation reaction} \\
O\_SHRINK = ( FXY(18,2) \ast Y(31) + FXY(18,5) \ast Y(32) \\
\& +FXY(18,6) \ast Y(33) + FXY(18,7) \ast Y(34) \\
\& +FXY(18,8) \ast Y(35) + FXY(18,9) \ast Y(36) \\
\& +FXY(18,10) \ast Y(37) + FXY(18,11) \ast Y(38) \\
\& +FXY(18,12) \ast Y(39) + FXY(18,13) \ast Y(40) \\
\& +FXY(18,14) \ast Y(41) + FXY(18,15) \ast Y(42) \\
\& +FXY(18,16) \ast Y(43) + FXY(18,17) \ast Y(44) \\
& ) \ast 0.1 \ast Y(19) \\

\textbf{C==== reactions in gas phase} \\
\textbf{C==== C6H6, C6H5, C12H10, C4H4, C4H3} \\
YP(1) = -R(1) -R(2) -R(3) -R(6) -R(9) -R(10) -R(11) \\
\& -R(12) +C6H6 \\
YP(2) = R(1) +R(2) -R(3) +2 \ast R(4) \\
\& -R(5) +R(9) +R(10) +R(11) +R(12) -R(13) \\
\& -FXY(1,3) \ast GROW2 \ast Y(2) \ast PNU(1) / (PNU(5) - PNU(3)) \\
\& -FXY(2,3) \ast GROW4 \ast Y(2) \ast PNU(2) / (PNU(5) - PNU(3)) \\
YP(3) = R(3) -R(4) \\
\& -FXY(1,4) \ast GROW2 \ast Y(3) \ast PNU(1) / (PNU(5) - PNU(4)) \\
\& -FXY(2,4) \ast GROW4 \ast Y(3) \ast PNU(2) / (PNU(5) - PNU(4)) \\
YP(4) = R(6) -R(8) \\
\& -FXY(2,3) \ast Y(4) \ast Y(2) - FXY(2,4) \ast Y(4) \ast Y(3) \\
\& -Y(4) \ast GROWTH4 \\
YP(5) = R(5) -R(7) \\
\& -FXY(2,3) \ast Y(5) \ast Y(2) - FXY(2,4) \ast Y(5) \ast Y(3) \\
\& -Y(5) \ast GROWTH4 \\

\textbf{C==== CH4, CH3, CH2, CH} \\
YP(6) = -R(14) -R(15) +R(17) +R(20) -R(25) -R(26) \\
\& -R(27) +CH4 \\
YP(7) = R(14) +R(15) +2 \ast R(16) -R(17) -R(20) +R(25) +R(26) \\
\& +R(27) -R(28) -R(29) +R(42) \\
YP(8) = R(45) -R(47) -R(48) \\
YP(9) = R(46) +R(48) -R(49) \\

\textbf{C==== C2H6, C2H5, C2H4, C2H3, C2H2, C2H, C2} \\
YP(10) = -R(16) -R(17) -R(18) -R(39) -R(40) +C2H6 \\
YP(11) = R(17) +R(18) -R(19) -R(20) +R(39) +R(40) -R(41)
\[
& - R(53) + H_2O
\]

\[
Y_P(22) = R(12) + R(26)
\]

\[
Y_P(23) = R(9) - R(12) - R(26) - R(37) + R(41)
\]

\[
Y_P(24) = - R(9) - R(13) + R(38) - R(41) - R(44) - R(49) - R(50)
\]

\[
Y_P(25) = 2R(13) + R(33) + R(34) + R(35) - R(36) \\
& - R(37) + R(38) + CO + R(45) + R(46) + R(47) \\
& + O\_SHRINK
\]

\[
Y_P(26) = R(36) + R(37) - R(38) + CO_2
\]

\[
Y_P(27) = R(30) + R(31) + R(32) - R(33) - R(34) - R(35) \\
& + R(42) + R(44) + R(49)
\]

\[
\]

\[
Y_P(29) = R(22) - R(22)
\]

\[
Y_P(30) = - R(55)
\]

C==== CO, CO_2, HCO, CH_2O

C==== Argon, VOLATILE

C==== Particles are divided into 14 classes: Y(31) ~ Y(44)

C A(I): the coagulation between smaller particles to produce particle-class I;
C B(I): the coagulation between smaller particle-classes and particle-class I to produce particle-class I+1;
C C(I): the coagulation between particle-class I and all the other greater particle-classes to produce respectively one more greater than those particle-classes themself.
C D(I): the oxidation of the particles. For specific particle I, oxidation shrinks particle-class I to particle-class I-1; and also oxidation shrinks particle-class I+1 to particle-class I.

\[
A(1) = (Y(14)Y(15) + Y(14)Y(16)) \times 1.0E-10
\]

\[
B(1) = FXY(1,2)GROW2Y(31)PNU(1)/(PNU(5)PNU(2)) \\
& + FXY(2,2)GROW4Y(31)PNU(2)/(PNU(5)PNU(2)) \\
C(1) = (FXY(2,2)Y(31) \\
& + FXY(2,5)Y(32) + FXY(2,6)Y(33) \\
& + FXY(2,7)Y(34) + FXY(2,8)Y(35) \\
& + FXY(2,9)Y(36) + FXY(2,10)Y(37) \\
& + FXY(2,11)Y(38) + FXY(2,12)Y(39)
\]
& \quad +FXY(2,13) \times Y(40) + FXY(2,14) \times Y(41)
& \quad +FXY(2,15) \times Y(42) + FXY(2,16) \times Y(43) \times Y(31)
\text{D}(1) &= FXY(18,5) \times Y(32) \times Y(31) \times Y(31) \times Y(19) \times 0.1/(\text{PNU}(5)-\text{PNU}(2))
& -FXY(18,2) \times Y(31) \times Y(31) \times Y(19) \times 0.1/(\text{PNU}(2))
\text{YP}(31) &= A(1) - B(1) - C(1) + D(1)

A(2) &= B(1) + FXY(2,2) \times (Y(31) \times 2) \times \text{PNU}(2)/(\text{PNU}(5))
& + \text{GROW2} \times Y(2) \times \text{PNU}(1)/(\text{PNU}(5) - \text{PNU}(3))
& + \text{GROW4} \times Y(2) \times \text{PNU}(2)/(\text{PNU}(5) - \text{PNU}(3))
& + \text{GROW2} \times Y(3) \times \text{PNU}(1)/(\text{PNU}(5) - \text{PNU}(4))
& + \text{GROW4} \times Y(3) \times \text{PNU}(2)/(\text{PNU}(5) - \text{PNU}(4)) \times 1.0 \times 10
B(2) &= (QXY(1,5) \times \text{GROW2} + QXY(2,5) \times \text{GROW4}
& +QXY(2,5) \times Y(31) \times Y(32)
C(2) &= (FXY(5,5) \times Y(32) + FXY(5,6) \times Y(33)
& +FXY(5,7) \times Y(34) + FXY(5,8) \times Y(35)
& +FXY(5,9) \times Y(36) + FXY(5,10) \times Y(37)
& +FXY(5,11) \times Y(38) + FXY(5,12) \times Y(39)
& +FXY(5,13) \times Y(40) + FXY(5,14) \times Y(41)
& +FXY(5,15) \times Y(42) + FXY(5,16) \times Y(43) \times Y(32)
D(2) &= FXY(18,6) \times Y(33) \times Y(19) \times 0.1/(\text{PNU}(6)-\text{PNU}(5))
& -FXY(18,5) \times Y(32) \times Y(19) \times 0.1/(\text{PNU}(5)-\text{PNU}(2))
\text{YP}(32) &= A(2) - B(2) - C(2) + D(2)

A(3) &= B(2) + QXY(5,5) \times Y(32) \times 2
B(3) &= (QXY(1,6) \times \text{GROW2} + QXY(2,6) \times \text{GROW4}
& +QXY(2,6) \times Y(31) + QXY(5,6) \times Y(32) \times Y(33)
C(3) &= (FXY(6,5) \times Y(33)
& +FXY(6,7) \times Y(34) + FXY(6,8) \times Y(35)
& +FXY(6,9) \times Y(36) + FXY(6,10) \times Y(37)
& +FXY(6,11) \times Y(38) + FXY(6,12) \times Y(39)
& +FXY(6,13) \times Y(40) + FXY(6,14) \times Y(41)
& +FXY(6,15) \times Y(42) + FXY(6,16) \times Y(43) \times Y(33)
D(3) &= FXY(18,7) \times Y(34) \times Y(19) \times 0.1/(\text{PNU}(7)-\text{PNU}(6))
& -FXY(18,6) \times Y(33) \times Y(19) \times 0.1/(\text{PNU}(6)-\text{PNU}(5))
\text{YP}(33) &= A(3) - B(3) - C(3) + D(3)

A(4) &= B(3) + QXY(6,6) \times Y(33) \times 2
B(4) &= (QXY(1,7) \times \text{GROW2} + QXY(2,7) \times \text{GROW4}
& +QXY(2,7) \times Y(31) + QXY(5,7) \times Y(32)
& +QXY(6,7) \times Y(33) \times Y(34)
C(4) &= (FXY(7,7) \times Y(34) + FXY(7,8) \times Y(35)
& +FXY(7,9) \times Y(36) + FXY(7,10) \times Y(37)
& +FXY(7,11) \times Y(38) + FXY(7,12) \times Y(39)
& +FXY(7,13) \times Y(40) + FXY(7,14) \times Y(41)
\[ A(5) = B(4) + QXY(7,7) \ast Y(34) \ast 2 \]

\[ B(5) = (QXY(1,8) \ast GROW2 + QXY(2,8) \ast GROW4 \]
\[ + QXY(2,8) \ast Y(31) + QXY(5,8) \ast Y(32) \]
\[ + QXY(6,8) \ast Y(33) + QXY(7,8) \ast Y(34) \ast Y(35) \]

\[ C(5) = (FXY(8,8) \ast Y(35) \]
\[ + FXY(8,9) \ast Y(36) + FXY(8,10) \ast Y(37) \]
\[ + FXY(8,11) \ast Y(38) + FXY(8,12) \ast Y(39) \]
\[ + FXY(8,13) \ast Y(40) + FXY(8,14) \ast Y(41) \]
\[ + FXY(8,15) \ast Y(42) + FXY(8,16) \ast Y(43) \ast Y(35) \]

\[ D(5) = FXY(18,9) \ast Y(36) \ast Y(19) \ast 0.1 / (PNU(9) - PNU(8)) \]
\[ - FXY(18,8) \ast Y(35) \ast Y(19) \ast 0.1 / (PNU(8) - PNU(7)) \]

\[ YP(35) = A(5) - B(5) - C(5) + D(5) \]

\[ A(6) = B(5) + QXY(8,8) \ast Y(35) \ast 2 \]

\[ B(6) = (QXY(1,9) \ast GROW2 + QXY(2,9) \ast GROW4 \]
\[ + QXY(2,9) \ast Y(31) + QXY(5,9) \ast Y(32) \]
\[ + QXY(6,9) \ast Y(33) + QXY(7,9) \ast Y(34) \]
\[ + QXY(8,9) \ast Y(35) \ast Y(36) \]

\[ C(6) = (FXY(9,9) \ast Y(36) + FXY(9,10) \ast Y(37) \]
\[ + FXY(9,11) \ast Y(38) + FXY(9,12) \ast Y(39) \]
\[ + FXY(9,13) \ast Y(40) + FXY(9,14) \ast Y(41) \]
\[ + FXY(9,15) \ast Y(42) + FXY(9,16) \ast Y(43) \ast Y(36) \]

\[ D(6) = FXY(18,10) \ast Y(37) \ast Y(19) \ast 0.1 / (PNU(10) - PNU(9)) \]
\[ - FXY(18,10) \ast Y(36) \ast Y(19) \ast 0.1 / (PNU(9) - PNU(8)) \]

\[ YP(36) = A(6) - B(6) - C(6) + D(6) \]

\[ A(7) = B(6) + QXY(9,9) \ast Y(36) \ast 2 \]

\[ B(7) = (QXY(1,10) \ast GROW2 + QXY(2,10) \ast GROW4 \]
\[ + QXY(2,10) \ast Y(31) + QXY(5,10) \ast Y(32) \]
\[ + QXY(6,10) \ast Y(33) + QXY(7,10) \ast Y(34) \]
\[ + QXY(8,10) \ast Y(35) + QXY(9,10) \ast Y(36) \ast Y(37) \]

\[ C(7) = (FXY(10,10) \ast Y(37) \]
\[ + FXY(10,11) \ast Y(38) + FXY(10,12) \ast Y(39) \]
\[ + FXY(10,13) \ast Y(40) + FXY(10,14) \ast Y(41) \]
\[ + FXY(10,15) \ast Y(42) + FXY(10,16) \ast Y(43) \ast Y(37) \]

\[ D(7) = FXY(18,11) \ast Y(38) \ast Y(19) \ast 0.1 / (PNU(11) - PNU(10)) \]
\[ - FXY(18,10) \ast Y(37) \ast Y(19) \ast 0.1 / (PNU(10) - PNU(9)) \]

\[ YP(37) = A(7) - B(7) - C(7) + D(7) \]
\[
\begin{align*}
A(8) &= B(7) + QXY(10, 10) \cdot Y(37)^2 \\
B(8) &= (QXY(1, 11) \cdot GROW2 + QXY(2, 11) \cdot GROW4 \\
& \quad + QXY(2, 11) \cdot Y(31) + QXY(5, 11) \cdot Y(32) \\
& \quad + QXY(6, 11) \cdot Y(33) + QXY(7, 11) \cdot Y(34) \\
& \quad + QXY(8, 11) \cdot Y(35) + QXY(9, 11) \cdot Y(36) \\
& \quad + QXY(10, 11) \cdot Y(37) \cdot Y(38) \\
C(8) &= (FXY(11, 11) \cdot Y(38) + FXY(11, 12) \cdot Y(39) \\
& \quad + FXY(11, 13) \cdot Y(40) + FXY(11, 14) \cdot Y(41) \\
& \quad + FXY(11, 15) \cdot Y(42) + FXY(11, 16) \cdot Y(43) \cdot Y(38) \\
D(8) &= FXY(18, 12) \cdot Y(39) \cdot Y(19) \cdot 0.1/(PNU(12) - PNU(11)) \\
& \quad - FXY(18, 11) \cdot Y(39) \cdot Y(19) \cdot 0.1/(PNU(11) - PNU(10)) \\
YP(38) &= A(8) - B(8) - C(8) + D(8) \\
A(9) &= B(8) + QXY(11, 11) \cdot Y(38)^2 \\
B(9) &= (QXY(1, 12) \cdot GROW2 + QXY(2, 12) \cdot GROW4 \\
& \quad + QXY(2, 12) \cdot Y(31) + QXY(5, 12) \cdot Y(32) \\
& \quad + QXY(6, 12) \cdot Y(33) + QXY(7, 12) \cdot Y(34) \\
& \quad + QXY(8, 12) \cdot Y(35) + QXY(9, 12) \cdot Y(36) \\
& \quad + QXY(10, 12) \cdot Y(37) + QXY(11, 12) \cdot Y(38) \cdot Y(39) \\
C(9) &= (FXY(12, 12) \cdot Y(39) \\
& \quad + FXY(12, 13) \cdot Y(40) + FXY(12, 14) \cdot Y(41) \\
& \quad + FXY(12, 15) \cdot Y(42) + FXY(12, 16) \cdot Y(43) \cdot Y(39) \\
D(9) &= FXY(18, 13) \cdot Y(40) \cdot Y(19) \cdot 0.1/(PNU(13) - PNU(12)) \\
& \quad - FXY(18, 11) \cdot Y(39) \cdot Y(19) \cdot 0.1/(PNU(11) - PNU(10)) \\
YP(39) &= A(9) - B(9) - C(9) + D(9) \\
A(10) &= B(9) + QXY(12, 12) \cdot Y(39)^2 \\
B(10) &= (QXY(1, 13) \cdot GROW2 + QXY(2, 13) \cdot GROW4 \\
& \quad + QXY(2, 13) \cdot Y(31) + QXY(5, 13) \cdot Y(32) \\
& \quad + QXY(6, 13) \cdot Y(33) + QXY(7, 13) \cdot Y(34) \\
& \quad + QXY(8, 13) \cdot Y(35) + QXY(9, 13) \cdot Y(36) \\
& \quad + QXY(10, 13) \cdot Y(37) + QXY(11, 13) \cdot Y(38) \\
& \quad + QXY(12, 13) \cdot Y(39) \cdot Y(40) \\
C(10) &= (FXY(13, 13) \cdot Y(40) + FXY(13, 14) \cdot Y(41) \\
& \quad + FXY(13, 15) \cdot Y(42) + FXY(13, 16) \cdot Y(43) \cdot Y(40) \\
D(10) &= FXY(18, 14) \cdot Y(41) \cdot Y(19) \cdot 0.1/(PNU(14) - PNU(13)) \\
& \quad - FXY(18, 13) \cdot Y(40) \cdot Y(19) \cdot 0.1/(PNU(13) - PNU(12)) \\
YP(40) &= A(10) - B(10) - C(10) + D(10) \\
A(11) &= B(10) + QXY(13, 13) \cdot Y(40)^2 \\
B(11) &= (QXY(1, 14) \cdot GROW2 + QXY(2, 14) \cdot GROW4 \\
& \quad + QXY(2, 14) \cdot Y(31) + QXY(5, 14) \cdot Y(32) \\
& \quad + QXY(6, 14) \cdot Y(33) + QXY(7, 14) \cdot Y(34) \\
& \quad + QXY(8, 14) \cdot Y(35) + QXY(9, 14) \cdot Y(36) \\
\end{align*}
\]
\& +QXY(10,14) \* Y(37) + QXY(11,14) \* Y(38) \\
\& +QXY(12,14) \* Y(39) + QXY(13,14) \* Y(40) \* Y(41) \\
C(11) = ( FXY(14,14) \* Y(41) \\
\& +FXY(14,15) \* Y(42) + FXY(14,16) \* Y(43) \) \* Y(41) \\
D(11) = FXY(18,15) \* Y(42) \* Y(19) \* 0.1/(PNU(15) - PNU(14)) \\
\& -FXY(18,14) \* Y(41) \* Y(19) \* 0.1/(PNU(14) - PNU(13)) \\
YP(41) = A(11) - B(11) - C(11) + D(11) \\

A(12) = B(11) + QXY(14,14) \* Y(41) \* 2 \\
B(12) = ( QXY(1,15) \* GROW2 + QXY(2,15) \* GROW4 \\
\& +QXY(2,15) \* Y(31) + QXY(5,15) \* Y(32) \\
\& +QXY(6,15) \* Y(33) + QXY(7,15) \* Y(34) \\
\& +QXY(8,15) \* Y(35) + QXY(9,15) \* Y(36) \\
\& +QXY(10,15) \* Y(37) + QXY(11,15) \* Y(38) \\
\& +QXY(12,15) \* Y(39) + QXY(13,15) \* Y(40) \\
\& +QXY(14,15) \* Y(41) \) \* Y(42) \\
C(12) = ( FXY(15,15) \* Y(42) + FXY(15,16) \* Y(43) \) \* Y(42) \\
D(12) = FXY(18,16) \* Y(43) \* Y(19) \* 0.1/(PNU(16) - PNU(15)) \\
\& -FXY(18,15) \* Y(42) \* Y(19) \* 0.1/(PNU(15) - PNU(14)) \\
YP(42) = A(12) - B(12) - C(12) + D(12) \\

A(13) = B(12) + QXY(15,15) \* Y(42) \* 2 \\
B(13) = ( QXY(1,16) \* GROW2 + QXY(2,16) \* GROW4 \\
\& +QXY(2,16) \* Y(31) + QXY(5,16) \* Y(32) \\
\& +QXY(6,16) \* Y(33) + QXY(7,16) \* Y(34) \\
\& +QXY(8,16) \* Y(35) + QXY(9,16) \* Y(36) \\
\& +QXY(10,16) \* Y(37) + QXY(11,16) \* Y(38) \\
\& +QXY(12,16) \* Y(39) + QXY(13,16) \* Y(40) \\
\& +QXY(14,16) \* Y(41) + QXY(15,16) \* Y(42) \) \* Y(43) \\
C(13) = ( FXY(16,16) \* Y(43) \) \* Y(43) \\
D(13) = FXY(18,17) \* Y(44) \* Y(19) \* 0.1/(PNU(17) - PNU(16)) \\
\& -FXY(18,16) \* Y(43) \* Y(19) \* 0.1/(PNU(16) - PNU(15)) \\
YP(43) = A(13) - B(13) - C(13) + D(13) \\

A(14) = B(13) + QXY(16,16) \* Y(43) \* 2 \\
B(14) = 0.0 \\
C(14) = 0.0 \\
D(14) = 0.0 \\
\& -FXY(18,17) \* Y(44) \* Y(19) \* 0.1/(PNU(17) - PNU(16)) \\
YP(44) = A(14) - B(14) - C(14) + D(14) \\

RETURN 
END

C==== end of yprime() function
output.f

C==== OUTPUT() calculate the particle distributed
C==== information, and output all those informations

SUBROUTINE OUTPUT(NEQ, NP, ISTEP, PNU, T_IN, Y, TEND)
INTEGER NEQ, NP, ISTEP
REAL *8 Y(NEQ), T_IN, TEND, PNU(NP)
INTEGER I
REAL *8 C_OUT, H_OUT, O_OUT
REAL *8 PI, AVOG, C(44), DIAM(15)
REAL *8 T_PAR, T_VOL, YAC, SUM1, SUM2, PER1, PER2,
&      DN, DV

AVOG        = 6.023D23
PI           = 3.14159

DO 51 I=1,NEQ
51      C(I) = Y(I)*AVOG

CGROW = C(4)+C(5)+C(13)+C(14)+C(15)+C(16)

C==== carbon balance
C_OUT = PNU(3)* (C(1)+C(2)) + PNU(4)*C(3)
& +PNU(2)* (C(4)+C(5))
& +PNU(1)* (C(10)+C(11)+C(12)+C(13)+C(14)+C(15)+C(16))
& +PNU(2)*C(31) + PNU(5)*C(32) + PNU(6)*C(33)
& +PNU(7)*C(34) + PNU(8)*C(35) + PNU(9)*C(36)
& +PNU(10)*C(37) + PNU(11)*C(38) + PNU(12)*C(39)
& +PNU(13)*C(40) + PNU(14)*C(41) + PNU(15)*C(42)
& +PNU(16)*C(43) + PNU(17)*C(44)

C==== hydrogen balance
H_OUT = 6.*C(1)+5.*C(2)+10.*C(3)+4.*C(4)+3.*C(5)
& +4.*C(6)+3.*C(7)+2.0*C(8)+C(9)
& +6.*C(10)+5.*C(11)+4.*C(12)+3.*C(13)+2.*C(14)+C(15)
& +C(17)+C(19)+2.*(C(20)+C(21)+C(22))+C(23)
& +C(27)+2.*C(28)
C==== oxygen balance
\[ O_{\text{OUT}} = C(18) + C(19) + C(21) + C(25) \]
& \[ + 2 \cdot (C(22) + C(23) + C(24) + C(26)) + C(27) + C(28) \]

write(*,*) ISTEP, TEND, T_IN*AVOG, O_OUT

\[ \text{DIAM}(1) = (6 \cdot \text{PNU}(2) \cdot (12 \cdot \text{AVOG}) / (2 \cdot \pi))^{0.3333} \cdot 1.0 \cdot 10^7 \]
DO 20 I = 2, 14
  \[ \text{DIAM}(I) = (6 \cdot \text{PNU}(I+2) \cdot (12 \cdot \text{AVOG}) / (2 \cdot \pi))^{0.3} \cdot 1.0 \cdot 10^7 \]
20 CONTINUE

T_PAR = 0.0
T_VOL = 0.0
SUM1 = 0.0
SUM2 = 0.0
YAC = 0.0

DO 10 I = 31, 44
  T_PAR = T_PAR + C(I)
10 CONTINUE

OPEN (UNIT=60, data/fort.60')

DO 50 I = 1, 14
  YAC = YAC + C(I+30)
  PER1 = YAC / T_PAR
  PER2 = C(I+30) / T_PAR
  T_VOL = T_VOL + C(I+30) * \pi * (\text{DIAM}(I) / 1.0 \cdot 10^7)^{3} / 6.0
  SUM1 = SUM1 + PER2 * \text{DIAM}(I)
  SUM2 = SUM2 + PER2 * \text{DIAM}(I)^{3}
  write(60,902) DIAM(I)
50 CONTINUE

DN = SUM1
DV = SUM2^{1/3}
CB = (1.85 * T_VOL * 1000.0 / 60.0) * 3600.0 / 1000.0

C === data used to discuss the results
write(11,902) TEND, C(1), C(24)
write(12,902) TEND, C(2), C(3), C(19)
write(21,902) TEND, DV, T_PAR, T_VOL, CB, DN
write(22,902) TEND, C(31), C(32), C(33)
C === general data output

902 FORMAT(E12.6,2X,E12.6,2X,E12.6,2X,E12.6,2X,E12.6,2X,E12.6,2X,E12.6)

RETURN
END

C==== end of OUTPUT()
SUBROUTINE REDO_CONC(NEQ, Y)
INTEGER NEQ
REAL *8 Y(NEQ)

INTEGER I
REAL *8 TOT_MOL, DELTA_Y, YNEW(30), YMOLE(30), TEMP, VOLUMN
REAL *8 VOLAT, FC6H6, FCH4, FC2H6, FH2O, FCO, FCO2, FH2
COMMON /A5/ VOLAT, FC6H6, FCH4, FC2H6, FH2O, FCO, FCO2, FH2
COMMON /A6/ TEMP, VOLUMN

TOT_MOL = 0.0
DELTA_Y = VOLAT - Y(30)

DO 10 I = 1, 29
   10 YNEW(I) = 0.0

   YNEW(1) = FC6H6 * DELTA_Y
   YNEW(6) = FCH4 * DELTA_Y
   YNEW(10) = FC2H6 * DELTA_Y
   YNEW(20) = FH2 * DELTA_Y
   YNEW(21) = FH2O * DELTA_Y
   YNEW(25) = FCO * DELTA_Y
   YNEW(26) = FCO2 * DELTA_Y

DO 20 I = 1, 29
   20 YMOLE(I) = Y(I) * VOLUMN + YNEW(I)
   TOT_MOL = TOT_MOL + YMOLE(I)
CONTINUE

DO 25 I = 31, 44
   25 YMOLE(I) = Y(I) * VOLUMN

VOLAT = Y(30)
VOLUMN = TOT_MOL * (82.06 * TEMP)
DO 30 I = 1, 29
   30 Y(I) = YMOLE(I) / VOLUMN
DO 35 I = 31, 44
   35 Y(I) = YMOLE(I) / VOLUMN

RETURN
END
# This makefile is used to compile all the functions and
# link all them together.

FFLAGS = -I/usr/local/vni/include

carbon2:    model_main.o initial.o rate_const.o coag_const.o  
            yprime.o heat_balance.o output.o redo_conc.o  
            f77 -g -o carbon       $(FFLAGS) model_main.o
initial.c  
            rate_const.o coag_const.o yprime.o  
            output.o redo_conc.o $(LINK_FNL)

# Compile all the functions
model_main.o: eq.f
    f77 -c -g $(FFLAGS) model_main.f $(LINK_FNL)
initial.o: initial.f
    f77 -c -g $(FFLAGS) initial.f $(LINK_FNL)
redo_conc.o: redo_conc.f
    f77 -c -g $(FFLAGS) redo_conc.f $(LINK_FNL)
rate_const.o: rate_const.f
    f77 -c -g $(FFLAGS) rate_const.f $(LINK_FNL)
coag_const.o: coag_const.f
    f77 -c -g $(FFLAGS) coag_const.f $(LINK_FNL)
yprime.o: yprime.f
    f77 -c -g $(FFLAGS) yprime.f $(LINK_FNL)
heat_balance.o: heat_balance.f
    f77 -c -g $(FFLAGS) heat_balance.f $(LINK_FNL)
output.o: output.f
    f77 -c -g $(FFLAGS) output.f $(LINK_FNL)

clean:
    rm -f *.o