Problems Involved in Simulating the
Flash Carbonization Process

A Thesis Presented to
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Ohio University

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of the Requirement for the Degree
Master of Science

By
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<th>Description</th>
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<td>Flash Carbonization Process</td>
</tr>
<tr>
<td>WCM</td>
<td>Wen and Chaung's Model</td>
</tr>
<tr>
<td>TEBPPG</td>
<td>Texaco Downflow Entrained-Bed Pilot Plant</td>
</tr>
<tr>
<td></td>
<td>Coal Gasifier</td>
</tr>
<tr>
<td>MAEROS</td>
<td>the Stand-Alone Multicomponent Aerosol</td>
</tr>
<tr>
<td></td>
<td>Module of CONTAIN</td>
</tr>
<tr>
<td>UCSM</td>
<td>Unreacted-Core Shrinking Model</td>
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1.1 Flash Carbonization Process

The Flash Carbonization Process (FCP), developed by Savage et al. (1), is an entrained-flow partial gasification process which produces concurrently a synthesis gas (hydrogen and carbon monoxide) and a low sulfur, low volatile char which is suitable for industrial and power plant use.

In 1986, Chen and Savage (2) modified this process to produce pure carbon blacks from coal. Synthesis gas was produced simultaneously because it was formed under the same operating conditions (high temperature, low pressure, and low oxygen to coal ratio) used in carbon black production.

The purpose of this study is to investigate some problems involved in simulating the FCP. Because the FCP produces both gaseous and solid products, it is necessary to predict both the yields of the synthesis gas and carbon blacks. This makes the simulation rather complicated. On the other hand, well-developed packages for both entrained-bed gasification and particle size calculation are available. Therefore, the major effort of this study was to use separate packages to predict both the product gas composition profiles and the carbon black particle size distribution, and compare the computational results with the experimental data.
1.2 Entrained-Bed Coal Gasification

Entrained-bed coal gasification involves the injection of fine coal, pulverized to a size of the order of 75 μm and suspended in a gas stream, into the gasifier burner to produce gaseous fuels of low to high heating values. Oxygen or air together with steam, is generally used as the gas stream to entrain the coal.

The most important feature of entrained-bed gasifiers is that as a group they operate at high temperatures under conditions where the coal slags in order to gasify the coal rapidly. A typical residence time is approximately five seconds. Due to this high temperature, all the volatiles are oxidized which leads to relatively high oxygen consumption. Furthermore, because most of the gasification reactions in the reactor are highly endothermic, a large amount of heat must be supplied either from the inside combustion reactions or from outside heat sources.

Tables 1 and 2 (36) list typical operating characteristics and product gas compositions for several entrained-bed gasification processes. Both commercial processes and those being demonstrated on a commercial scale are included.
Table 1 Typical Operating Characteristics of Entrained Flow Gasifiers Using Bituminous Coals and Blown with Oxygen or Air

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Steam/O₂</th>
<th>Water/O₂</th>
<th>Steam/Air</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Koppers-</td>
<td>(Texaco)²</td>
<td>(Foster</td>
<td>(Combustion</td>
</tr>
<tr>
<td></td>
<td>Totzek)</td>
<td>$</td>
<td>Wheeler)</td>
<td>Engineering)</td>
</tr>
<tr>
<td>Pressure, MPa</td>
<td>0.13</td>
<td>4.0</td>
<td>2.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Combustion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas Exit</td>
<td>1925</td>
<td>1400</td>
<td>1370-1450</td>
<td>1750</td>
</tr>
<tr>
<td>Steam (water)/Oxidant, Kg/Kg</td>
<td>0.4</td>
<td>0.5</td>
<td>0.05</td>
<td>0</td>
</tr>
<tr>
<td>Oxidant, Kg/GJ gas</td>
<td>52</td>
<td>37</td>
<td>111</td>
<td>139</td>
</tr>
<tr>
<td>Coal Residence Time, Sec.</td>
<td>1</td>
<td>3</td>
<td>N/A</td>
<td>2.5</td>
</tr>
<tr>
<td>Coal Gas Efficiency, %</td>
<td>75</td>
<td>75</td>
<td>90</td>
<td>69</td>
</tr>
</tbody>
</table>

* Lower Stage
$ Low Water Feed Case
@ After Quenching
# Upper Stage
N/A Not Available
Table 2 Typical Product Gas Composition* in Mole Percent from Gasification of 
Bituminous Coals in Entrained Flow Gasifiers Blown with Oxygen or Air

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Steam/O₂</th>
<th>Water/O₂</th>
<th>Steam/Air</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Koppers-</td>
<td>(exaco)</td>
<td>(Foster</td>
<td>(Combustion</td>
</tr>
<tr>
<td></td>
<td>Totzek)</td>
<td></td>
<td>Wheeler)</td>
<td>Engineering)</td>
</tr>
<tr>
<td>CO₂</td>
<td>10</td>
<td>12</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>CO</td>
<td>53</td>
<td>52</td>
<td>29</td>
<td>23</td>
</tr>
<tr>
<td>H₂</td>
<td>36</td>
<td>35</td>
<td>15</td>
<td>12</td>
</tr>
<tr>
<td>N₂</td>
<td>-</td>
<td>-</td>
<td>49</td>
<td>59</td>
</tr>
<tr>
<td>Other</td>
<td>1</td>
<td>1</td>
<td>4@</td>
<td>1</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

* Dry Basis After Scrubbing and Cooling
@ Mostly Methane
1.3 Carbon Black Growth

Carbon black particles are believed to form in the early stages of the FCP. After the formation, some particle growth processes are involved to increase the particle size of carbon blacks.

The particle size distribution of aerosols can be shaped by both the coagulation process and the gas-to-particle conversion process. Coagulation refers to particles sticking together due to particle-particle collisions. The size of new particles thereby increases. The number of particles will be reduced by this process but the total mass will remain the same.

Gas-to-particle conversion may be either derived from homogeneous gas phase processes or controlled by processes in the particulate phase. Gas-phase processes can produce a supersaturated state which then collapses due to the formation of aerosols. Once a condensable species has been formed in the gas phase, the system is in an unstable state. It may pass toward the equilibrium condition either by the generation of new nuclei or by condensation on existing particles. This process changes not only the particle size distribution but also the total mass of particles.

1.4 Simulation Approach

The works of this study were primarily based on two computer packages. The first one is the "Entrained-Bed Coal
Gasification Modelling developed by Wen and Chaung (3), and the second one is a package, the stand-alone multicomponent aerosol module of CONTAIN (MAEROS), which calculates aerosol composition and mass concentration as a function of particle size and time. The detailed description of the latter package can be obtained in the user's manual published by Sandia National Laboratories (4). Wen and Chaung's Model (WCM) was used to predict the product gas compositions and the MAEROS was used to calculate the size distribution of carbon black.

In the original WCM, the gasifier was conceptually divided into three zones: (1) the pyrolysis and volatiles combustion zone; (2) the char combustion and gasification zone; and (3) the gasification and secondary gas reaction zone. These three zones of reactions were assumed to take place sequentially (i.e., after the pyrolysis and volatiles combustions were completed, the char combustion took place; and gasification happened when combustion ended). Because the amount of oxygen supplied in the FCP, all of the oxygen was consumed before the end of pyrolysis. Therefore, in this study, although the three zones were still assumed, there was actually no second zone and the reactions in the third zone were considered to be able to take place simultaneously with pyrolysis immediately after the oxygen was consumed. Along with this, some modifications on the original WCM model were made, including the correction of
the mass balance in the pyrolysis stage. Different kinetic models for pyrolysis, char-carbon dioxide reaction and methane-water reforming reaction were incorporated into the WCM. The computational results of this proposed model were compared with the experimental data. The new model accurately predicted trends in experimentally observed product gas compositions.

The MAEROS package was run separately. Although the available experimental information concerning the carbon black production was very limited, based on some assumptions, the average particle size of the carbon black was still obtained and was close to the instrument-analyzed results.

Suggestions of how to integrate these two computer programs are proposed.
CHAPTER TWO
LITERATURE REVIEW

2.1 Process Description of the FCP

The FCP apparatus was first reported by Savage et al. (5) as shown in Figure 1. A 160 cm long, 10 cm diameter flanged pipe is used as the entrained-flow reactor. Three zones of 46 cm heaters are used to maintain the isothermal temperature, initiate the reactions, and offset the heat loss. Table 3 shows the typical operating conditions.

Table 3. Typical Operating Conditions For FCP

<table>
<thead>
<tr>
<th>Feed</th>
<th>1.9 kg/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>5 liter/min</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>5 liter/min</td>
</tr>
<tr>
<td>Water</td>
<td>2 cc/min</td>
</tr>
<tr>
<td>Isothermal Temperature</td>
<td>1450 °K</td>
</tr>
<tr>
<td>Pressure</td>
<td>1 atm</td>
</tr>
</tbody>
</table>

The reactor is preheated to the desired temperature with a small flow of nitrogen gas through the feed nozzle. When the temperature remains constant, water is introduced through a steam generator at the desired rate and the flow of oxygen is adjusted in the annular space of the feed nozzle. The pulverized coal (about 250 μm in diameter) is
FIGURE 1. THE FLASH CARBONIZATION UNIT
fed by the vibra screw feeder through the center tube with nitrogen and the reactions take place.

The fine and pure carbon black particles, entrained by the product gas, are separated in the bag house separator and char is collected in a collector at the bottom of the reactor. Product gas leaving the bag house is sampled at intervals and is analyzed by a gas chromatograph.

2.2 Reactions in Flash Carbonization Reactor

In the experiment using the FCP, pulverized coal particles are entrained in a downward stream of oxygen, nitrogen, and steam. As the particles travel along the reactor, they are successively devolatized, burned, and gasified. The chemical reactions involved can be classified as a combination of pyrolysis (devolatilization) & carbonization, combustions, gasification & secondary gaseous reactions, and particle growth. Each possible chemical reaction and its kinetics in the FCP reactor are described as follows:

2.2.1 Pyrolysis

Coal, consisting of C, H, O, N, S, and ash, is a very complex compound. When it is heated to about 350°C, it begins to decompose, releasing various volatiles including CO₂, CO, CH₄, N₂, H₂, H₂S, tar, and other hydrocarbons. The amount and distribution of the products strongly depend
on the type of coal and operating conditions, such as pressure, temperature, heat rate, etc.

The chemical equation for the devolatilization reaction can be represented as follows:

\[ C_{\alpha \beta \gamma \delta \epsilon_i}H_{\alpha_i}O_{r_i}N_{S_i}S_{A} \rightarrow C_{\alpha \beta \gamma \delta \epsilon_i} + \text{Volatile(CO, H}_2\text{, CO}_2\text{, CH}_4\text{, H}_2S\text{, N}_2\text{, Tar)} \] [1]

The composition of tar is very complex. It contains a large number of different aromatic compounds and is sometimes simply represented as benzene, C6H6 for modelling purposes.

Carbon black is formed by partial combustion or pyrolysis of many organic substances. Basically, it is composed of elemental carbon in the form of non-spherical particles of colloidal sizes, which are coalesced into particle aggregates obtained by partial combustion or thermal decomposition of hydrocarbons. The possible carbon black formation reactions due to pyrolysis in the FCP include:

\[ \text{(1) } C_{6}H_{6} \rightarrow 6 \text{ C} + 3 \text{ H}_2 \] [2]
\[ \text{(2) } \text{CH}_4 \rightarrow \text{ C} + 2 \text{ H}_2 \] [3]

The rate and degree of devolatilization of coal depend strongly on the type of coal and operating conditions. Experimental data show that volatile yield increases significantly with decreasing pressure, increasing hydrogen partial pressure, as the final temperature of the particle increases, and as the heat rate is increased. Due to these
factors, many devolatilization models have been proposed, including simple single-step unidirectional decomposition, series decompositions, two competing unidirectional decompositions, and multi-step series competition model, as summarized by Anthony and Howard (6).

It is known that the thermal decomposition of simple organic species is described as a first-order reaction in the amount of unreacted material remaining. Based on this concept, Badzioch & Hawksley (7), Anthony & Howard (6), and Wen et al. (8) represented the devolatilization process as a first-order decomposition occurring uniformly throughout the coal with the rate of volatile yield assumed to be proportional to the remaining volatile matter in coal:

\[ \frac{dV}{dt} = k \cdot (V^* - V) \] (g/sec) \[4\]

where \( V \) is the volatile matter evolved and \( V^* \) is the total amount of volatile matter evolved after a long period of time. \( V \rightarrow V^* \) as \( t \rightarrow \infty \). The rate constant, \( k \), can be correlated by the Arrhenius expression:

\[ k = k_0 \cdot \exp\left(\frac{-E}{R \cdot T_s}\right) \] \[5\]

where \( T_s \) is the solid temperature in °K and \( E \) is the activation energy.

For Badzioch & Hawksley (7) and Wen et al. (8), the activation energy, \( E \), is taken as constant. According to Badzioch & Hawksley (7), \( E \) equals 17.8 Kcal/mole for ten types of coal. Anthony & Howard (6) reported the value of
the activation energy from 2 to 50 Kcal/mole depending on coal type and operating conditions.

The pressure effect was also studied by Anthony and Howard (6). After considering the competition between diffusional escape and the secondary reaction of reactive volatile species (primarily tarry compounds), they proposed an expression:

\[ V^* = V^*_{nr} + \frac{V^{**}}{n_r \left(1 + k_1 \cdot \frac{P_t}{k_c}\right)} \]  

where \( V^*_{nr} \) is the potential ultimate yield of volatile at very high pressure (greater than 100 atms)

\( V^{**} \) is the portion of volatile which exceeds \( V^*_{nr} \) at very low pressure (less than 0.001 atm)

\( k_c \)
\( \frac{k_c}{P_t} \) is the overall mass transfer coefficient

\( P_t \) is the total pressure in atm.

\( k_1 \)
\( \frac{k_1}{k_c} \) is taken as 0.56.

This equation fitted the data accumulated over a pressure range of 0.001 to 100 atmospheres for some types of coal. Wen and Chaung (3) used a linear interpolation over some experimental data at 1 atm and obtained an equation:

\[ V^* = V^*_{(at 1 \text{ atm})} \cdot (1 - a \cdot \ln(P_t)) \]  

where a is calculated as 0.086 for bituminous coals. This equation is valid if the pressure of the gasifier is between 0.1 and 50 atmospheres.
The production of carbon from coal was first reported by Johnson et al. (9). Opinions regarding the mechanism of carbon black formation vary considerably: Ray & Long and Street & Thomas separately suggested that the formation of carbon black involves the process of both aggregation and dehydrogenation; Smith proposed that the fuel molecules first undergo dehydrogenation giving the C2 radicals which then condense to give carbon black; Wolfhard and Parker thought that fuel molecules initially polymerize giving rise to saturated polymers which are then dehydrogenated to yield carbon black, as summarized by Haque et al. (10). Lahaye and Prado (11) studied the formation of carbon black by thermal treatment of hydrocarbons in the absence of oxygen, as well as by their partial combustion. They concluded that it appears to be that the initial hydrocarbon is being transformed by complex reactions into large polyaromatic molecules which condense into liquid microdroplets, precursors of the ultimate carbon black particles.

The kinetics of carbon black formation in both pyrolysis and partial combustion systems is not known. The reason for the difficulty in studying the kinetics is that the carbonization is usually completed within a few milliseconds.

2.2.2 Combustion Reactions

When coal is pyrolyzed, hydrogen-rich volatiles are
distilled and a solid residue, char, is left behind. Char, containing mainly carbon and the original mineral matters in coal, differs from the original coal in density, particle size, shape, and porosity.

Because the presence of oxygen, the devolatized char, combustible volatiles, and carbon blacks undergo combustion reactions and produce CO₂ and H₂O as the major products. However, partial combustions of hydrocarbons, CH₄ and Tar, are also possible to take place to form carbon blacks. The chemical equations can be summarized as follows:

(1) **Char-Oxygen Combustion**

\[
C_{\alpha}H_{\beta}O_{\gamma}N_{\delta}S_{\epsilon}A + \left( \frac{\alpha}{\phi} - \frac{\beta}{4} + \frac{\gamma}{2} - \frac{\delta}{2} \right) O_2 \rightarrow 2(1 - \frac{1}{\phi})\alpha CO + (\frac{\beta}{\phi} - 1)\alpha CO_2 + (\frac{\gamma}{2} - \epsilon) H_2O + \frac{\delta}{2} N_2 + \epsilon H_2S + Ash \quad [8]
\]

(2) \( H_2 + \frac{1}{2} O_2 \rightarrow H_2O \quad [9] \)

(3) \( CO + \frac{1}{2} O_2 \rightarrow CO_2 \quad [10] \)

(4) \( CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O \quad [11] \)

(5) \( C_6H_6 + \frac{15}{2} O_2 \rightarrow 6 CO_2 + 3 H_2O \quad [12] \)

(6) \( C \text{ (carbon black)} + \frac{1}{2} O_2 \rightarrow CO_2 \quad [13] \)

(7) \( C_6H_6 + \frac{3}{2} O_2 \rightarrow 6 C + 3 H_2O \quad [14] \)

(8) \( CH_4 + O_2 \rightarrow C + 2 H_2O \quad [15] \)

\( \phi \), in equation [8], is the mechanism factor which represents the number of moles of carbon consumed per mole of oxygen in the combustion reaction. When \( \phi \) equals 1, CO₂
is the only product while CO is the only product when $\phi$ equals 2. The kinetics of char-gas reactions, including char combustion and char gasification reactions (listed in next section), involves mass transfer between gas and solid phases, and is very complicated. The Unreacted-Core Shrinking Model (UCSM) (12), in which the effects of the diffusion and the chemical reactions are considered, is applied to calculate the reaction rates of these char-gas reactions. The detailed discussions of UCSM and kinetic models for different reactions are given in next chapter.

2.2.3 Gasification, Secondary Gaseous Reactions, and Carbon Black Growth

When oxygen is consumed, char and carbon black react with steam, carbon dioxide, and hydrogen to form CO, H$_2$, and CH$_4$. These reactions, known as gasification reactions, are shown as follows:

(1) Char-Steam Reaction:

\[
C_{\alpha \beta \rho \gamma \delta \varepsilon \zeta A} + (\alpha - r) \text{H}_2\text{O} \rightarrow \alpha \text{CO} + \\
(\alpha - r + \frac{6}{2} - \delta) \text{H}_2 + \varepsilon \text{H}_2\text{S} + \frac{6}{2} \text{N}_2 + \text{Ash}
\]

(2) Char-Carbon Dioxide Reaction:

\[
C_{\alpha \beta \rho \gamma \delta \varepsilon \zeta A} + \alpha \text{CO}_2 \rightarrow 2\alpha \text{CO} + \frac{r}{2} \text{H}_2\text{O} + \\
(\frac{8}{2} - \varepsilon - r) \text{H}_2 + \varepsilon \text{H}_2\text{S} + \frac{8}{2} \text{N}_2 + \text{Ash}
\]

(3) Char-Hydrogen Reaction:

\[
C_{\alpha \beta \rho \gamma \delta \varepsilon \zeta A} + (2\alpha + r + \varepsilon - \frac{8}{2}) \text{H}_2 \rightarrow \alpha \text{CH}_4 +
\]
17

\[ r \, H_2O + \varepsilon \cdot H_2S + \frac{5}{2} \, N_2 + \text{Ash} \]

(4) **Carbon Black-Steam Reaction**

\[ C \text{ (carbon black)} + H_2O \rightarrow CO + H_2 \]

(5) **Carbon Black-Carbon Dioxide Reaction**

\[ C \text{ (carbon black)} + CO_2 \rightarrow 2 \, CO \]

(6) **Carbon Black-Hydrogen Reaction**

\[ C \text{ (carbon black)} + 2 \, H_2 \rightarrow \text{CH}_4 \]

In addition to the gasification reactions, three gas phase secondary reactions are taken into consideration. They are the water-gas-shift reaction, the methane-steam-reforming reaction, and the methane-carbon dioxide-reforming reaction, respectively. The reaction equations can be represented as follows:

(7) **Water-Gas-Shift Reaction**:

\[ CO + H_2O \leftrightarrow CO_2 + H_2 \]

(8) **Methane-Water-Reforming Reaction**:

\[ \text{CH}_4 + H_2O \leftrightarrow CO + 3 \, H_2 \]

(9) **Methane-Carbon Dioxide-Reforming Reaction**:

\[ \text{CH}_4 + CO_2 \leftrightarrow 2 \, CO + 2 \, H_2 \]

The water-gas-shift reaction is the most widely employed reaction in industry to adjust the ratio of hydrogen to carbon monoxide for synthesis gas production. This reaction is reversible and is very fast in the presence of catalyst. Almost all the commercial catalysts for this reaction are made from iron-oxides with Cr2O3 used as a
stabilizer. In a coal gasifier, the water-gas-shift reaction is strongly catalyzed by the ash content of the char because a significant amount of Fe₂O₃ and other mineral matter, which serve as the catalysts, is found in ash.

The water-gas-shift reaction has been well studied. Both first-order and second-order rate equations have been reported. Singh and Saraf (13) proposed a first-order rate equation, taking into consideration the effect of temperature, pressure, age of catalyst, and H₂S content in the reacting gases on a catalyst, for simulation of the high temperature water-gas-shift reaction. Good agreement was found between the experimental data and the calculated results. After some modifications, this can be applied to estimate the rate of the water-gas-shift reaction in a coal gasifier. The equation is:

\[
\text{rate} = F_w \cdot 2.877 \times 10^5 \cdot \frac{1}{P_t} \cdot (P_{\text{CO}} - \frac{P_{\text{CO}_2} \cdot P_{\text{H}_2}}{k_{eq} \cdot P_{\text{H}_2}O}) \cdot \exp\left(-\frac{27760}{1.987 \cdot T_s}\right) \cdot P_f \cdot R_a(T), \text{gmole/(sec\cdot g ash)} \quad [25]
\]

where \(k_{eq} = \exp(-3.6839 + \frac{7234}{1.8 \cdot T_m})\) \quad [26]

\(k_{eq}\) is the equilibrium constant of this reaction

\(P_f = P_t \cdot 0.5 - \frac{250}{P_t}\) \quad [27]

is the pressure correcting factor

\(F_w\) is the catalyst reactivity correcting factor.

The rate is defined as the change of number of moles of CO per gram of ash per unit time.
The methane-water-reforming reaction is a reversible reaction and is believed to be catalyzed by the minerals in coal. Due to the important industrial application in manufacturing synthesis gas, this reaction has been extensively investigated.

Aker et al. (14) proposed that the rate is first order with respect to the methane partial pressure. Bordrov et al. (15) studied this reaction in the temperature range between 1090°C and 1170°C at atmospheric pressure using a nickel foil as the catalyst to eliminate the pore diffusion in catalyst particles. They concluded the reaction is retarded by both the carbon monoxide partial pressure and the ratio of steam pressure to hydrogen pressure. They revised Aker's model and proposed the following rate equation:

\[
\text{rate} = k \cdot P_{CH_4} \cdot \theta
\]  

where \( \theta = \frac{1}{1 + a \cdot \frac{P_{H_2O}}{P_{H_2}} + b \cdot P_{CO}} \)  

\( \theta \) is the fraction of free surface on char  
\( k \) is the rate constant, g mole/(sec*atm*g ash)  
a, b: parameters, function of temperature  
at 800°C \( a = 0.5 \) \( b = 2.0 \)  
at 900°C \( a = 0.2 \) \( b = 0 \).

At temperatures above 1200°C, the rate of decomposition of \( CH_4 \) is almost independent of its partial pressure and the ratio of steam pressure to hydrogen pressure, i.e. \( a = 0 \).
and $b = 0$. The reaction then becomes first-order.

The methane-carbon dioxide reforming reaction is fairly rapid in the presence of a catalyst. However, Sheu (16) found that this reaction is not appreciable up to 1170°C in the presence of ash, which is the catalyst in coal gasifier. Therefore the effect of the carbon dioxide-methane-reforming reaction can be ignored.

Carbon black particles begin to grow in size when oxygen is consumed. Two processes, the coagulation process and gas-to-particle conversion process, are possible to shape the particle size distributions.

Lahaye and Prado (11) also studied the growth process of carbon black and concluded that the growth consists of simultaneous coagulation of small nuclei and deposit of large polyaromatic molecules on their surfaces. However, the real growth process of carbon blacks involved in the FCP reactor is not clear.

2.3 The Significance of Previous Work

In 1978, Wen and Chaung (3) developed a mathematical model to simulate the Texaco Downflow Entrained-Bed Pilot Plant Coal Gasifier (TEBPPG) using coal liquefaction residues and coal-water slurries as feedstocks. This was a steady-state, one-dimensional model. The mixing in the gas phase was assumed to be complete at the entrance region which is followed by a region approximating plug flow. The
solid phase was assumed to be a plug flow throughout the reactor. The kinetics of all reactions involved, transport rates, and hydrodynamics were also taken into consideration. The product gas composition profiles and temperature profiles along the reactor were obtained by solving the mass balance and energy balance of the system. The major effort of WCM has been focused on the simulation of the experimental results. Very good agreement was obtained between the computational results from the model and experimental data from TEBPPG tests.

The performance of the TEBPPG under different operating conditions was also studied. They concluded:

(1) The carbon conversion can be significantly increased by increasing the oxygen/fuel (residue or coal slurry) ratio.

(2) For a given oxygen/fuel ratio, there is an optimum ratio of steam/fuel which maximizes the carbon conversion for system using steam rather than water in the feedstocks.

(3) The concentration of H₂ and CO₂ increases when the ratio of steam/fuel increases, but the concentration of CO decreases in this situation.

(4) Increasing the oxygen/fuel ratio slightly decreases the H₂ concentration, while it increases the CO concentration in product gas.
However, the influence is very limited.

(5) Carbon conversion can be increased by increasing the operating pressure.

(6) Small particles give a high carbon conversion for a given mass feed rate.

2.4 The Significance of This Study

The development of the model for the FCP was based primarily on WCM. In this study, it has been proved that WCM was limited to TEBPPG only. Errors from mass balance were introduced when this model is directly applied to the FCP. Therefore, some modifications were made to fit the experimental data from the FCP. Detailed discussions about the mistakes which resulted from WCM and the modifications made are given in chapter four. The new model developed for this study is more general, i.e. it can be used to predict the product gas distribution for both processes.

Based on limited experimental data, several assumptions were made when using the MAEROS package. A close computational average particle size was obtained. Detailed discussion on the assumptions and results are given in chapters three and four.
CHAPTER THREE
MATHEMATICAL MODELLING

The chemical reactions involved in the FCP reactor can be classified as a combination of pyrolysis (devolatilization) & carbonization, combustion, gasification & secondary gaseous reactions, and particle growth. Based on the above consideration, the gasifier can be conceptually divided into three zones:

(1). pyrolysis, volatile combustion and carbonization zone
(2). char combustion and gasification zone
(3). char gasification, secondary gaseous reactions, and carbon black growth zone

Figure 2 shows the three zones schematically.

In this chapter, the suitable kinetic models for the reactions in each zone are selected. The hydrodynamic and energy and mass balances are also discussed.

3.1 Kinetics in Flash Carbonization Process

The kinetics of each reaction involved in a entrained-bed coal gasifier has been studied by many researchers. In the following sections, suitable kinetic models for each reaction are selected for the modelling of the FCP.
FIGURE 2. THREE ZONES IN THE FLASH CARBONIZATION REACTOR
3.1.1 Pyrolysis

It is unfortunate that the experimental data on pyrolysis of the Ohio Clarion 4A coal used in the FCP are not available. The values of both \( k_0 \) and \( E \) must, therefore, be chosen from the reported data. The rate equation suggested by Anthony and Howard (6) for Pittsburgh bituminous coal was selected for this study because the volatile content of Pittsburgh bituminous coal is close to that of Ohio Clarion 4A (6, 2). The equation can be represented as:

\[
\frac{dv}{dt} = 1.8 \cdot 10^3 \cdot \exp\left(-\frac{13300}{1.987 \cdot Ts}\right) \cdot (V^* - V) \quad [30]
\]

Since the FCP was operated under atmospheric pressure, the effect of pressure, according to equation [7], can be neglected.

It is rather difficult to estimate the composition of volatiles because it varies with different types of coal, operating conditions, and solid residence times. Wen and Chaung (3) summarized the experiments done by Loison and Chauvin by diagramming the plot shown in Figure 3. This plot was used to estimate the volatile composition for the FCP.
FIGURE 3. PRODUCT YIELDS OF COAL PYROLYSIS, SUMMARIZED FROM DATA OF LOISON AND CHAUVIN BY WEN AND CHAUNG (3)
3.1.2 Volatile Combustion and Carbonization

In a typical entrained-bed gasification process, the amount of oxygen supplied is sufficient to burn all the volatiles released from coal into CO₂ and H₂O at the operating temperature, except N₂ and H₂S. But for the FCP, the oxygen-to-coal ratio in the feed was too low to burn all volatiles. Therefore, care must be taken when considering the volatile combustions. The difference which resulted from insufficient oxygen in programming is discussed below.

Volatile combustions burn with oxygen either immediately after leaving the coal particles or after the volatile jets have reached a distance from the particle. Howard and Essenhigh (17) suggested that volatile combustion happens simultaneously both in the interior of the solid and in the laminar layer of gas surrounding the particle. Field et al. (18) assumed that the overall rate is probably controlled by the boundary layer diffusion based on the facts that oxygen mixes with volatiles on the particle surface and that the rate of burning is very fast. Dobnor et al. (19) proposed that combustion of volatiles takes place in the laminar layer surrounding the particle and that oxygen can not reach the interior of the particle until the outside combustion is complete. Based on an assumption that the volatiles become CO and H₂O first with the subsequent CO oxidation as the rate controlling step, Hottel et al. (20) calculated the CO oxidation rate at about 1500°C and concluded that the CO
combustion rate is about $10^5$ times greater than the subsequent combustion rate of char and oxygen. Therefore, char combustion does not have significance until devolatilization ends.

In the original computer program of WCM, devolatilization was considered to be complete before the volatile combustions began. In other words, it calculated the total amount of volatiles produced first, then calculated the consumption of oxygen and the amount of CO$_2$ and H$_2$O produced. Because the amount of oxygen supplied to the TEBPPG was always more than enough to burn all the combustible volatiles, this algorithm did not cause any problem. Yet for the FCP, the insufficiency of oxygen in the feed causes Wen and Chaung's program to be inaccurate on the mass balance for the volatile combustion calculation. More CO$_2$ and H$_2$O than the maximum amounts allowed were always generated. Therefore, in the development of this model, volatile combustions were considered to happen continuously right after any small amount of volatiles were released from the coal, until either the devolatilization was complete or all oxygen was consumed. Then the subsequent char-gas and secondary gaseous reactions took place.

One assumption was made on the "order" in which combustible volatiles released from devolatilization react with oxygen. Tar was assumed to burn first, then CO and H$_2$; CH$_4$ was assumed the least combustible. This assumption may not
be accurate, but its effect will be negligible since the incremental difference in the amount of volatiles along the reactor length is fairly small during the devolatilization.

Since the kinetics of carbon black formation in both pyrolysis and partial combustion systems is not known, assumptions must be made in order to calculate the amount of carbon blacks produced. In the experiments using the FCP, tar was never detected in either the gas or solid products. It is thus assumed here that, after all the oxygen was consumed, carbon black was formed by thermal cracking of tar according to equation [2]:

\[ C_6H_6 \rightarrow 6\ C + 3\ H_2 \]  

[2]

Methane is another possible source of carbon black as discussed in the previous chapter. Since the portion of methane that is converted to carbon black is not known, equations [14] and [15] are not taken into consideration as other sources of carbon black.

3.1.3 Char-Gas Reactions

In the second and third zones, char undergoes several heterogeneous reactions including the char-oxygen reactions, char-steam reactions, char-carbon dioxide reactions, and char-hydrogen reaction. These reactions can be classified into two types: volumetric reactions and surface reactions.

In the case of volumetric reactions, chemical reactions take place throughout the interior of the particle as the
gas diffuses into the interior of the particle. The intrinsic reaction rate of the volumetric reactions is usually the rate-controlling step because the diffusion rate is much faster. In the surface reaction, on the other hand, gas, instead of diffusing into the interior of the particles, reacts at the surface of the solid or at the interface between the unreacted solid and the porous product ash layer. The chemical reaction is usually very rapid and the diffusion is sufficiently slow to become the rate-controlling step.

For temperatures below 1000°C, char-steam reactions, char-carbon dioxide reactions, and char-hydrogen reactions are usually slow and take place according to the volumetric reaction. For temperatures higher than 1100°C, except in char-hydrogen reactions, the diffusion of the reacting gas through the gas film and ash layer becomes dominant. In the typical operating conditions of the FCP, the temperature is about 1450°K; therefore, diffusion is considered to be the controlling factor in the gasification.

Since the solid loading in the FCP is less than 0.1% of the reactor volume, the collisions between particles can be neglected and the ash layer formed on the outside of the particle is assumed to be able to remain on the particle throughout the reaction. Thus the Unreacted-Core Shrinking Model, in which the effects of the diffusion and the chemical reactions are considered, is applicable in calcu-
lating the reaction rate of these char-gas reactions. The overall rate constant is:

\[
k_{\text{over}} = \frac{1}{k_{\text{dg}}} + \frac{1}{k_{\text{dash}}} \left( -\frac{Y}{Y_s} \right) + \frac{1}{Y_s k_s}
\]  \[31\]

where

\[
Y = \frac{r_c}{R}
\]

\[r_c\] is the radius of the unreacted-core
\[R\] is the radius of the whole particle including the ash layer

\[k_{\text{dg}}\] is the gas film diffusion constant, \(g/(cm^2\text{atm sec})\)
\[k_s\] is the surface reaction constant, \(g/(cm^2\text{atm sec})\)
\[k_{\text{dash}}\] is the ash diffusion constant, \(g/(cm^2\text{atm sec})\)

The unit of \(k_{\text{over}}\) is \(g/(cm^2\text{atm sec}).\) The overall rate equation can be expressed as:

\[
\text{rate} = k_{\text{over}} \cdot (P_i - P_i^*)
\]  \[32\]

where rate is defined as the mass of carbon consumed per unit surface area of particles per unit time 
\((P_i - P_i^*)\) is the effective partial pressure of the gas taking account of the reverse reaction effect

The ash diffusion rate constant, \(k_{\text{dash}}'\) can be roughly estimated by (3):

\[
k_{\text{dash}} = k_{\text{dg}} \cdot \varepsilon^{2.3}
\]  \[33\]

where \(\varepsilon\) is the voidage of the ash layer and is selected to be 2.5.

The individual kinetics of each char-gas reaction is
discussed in the following sections.

3.1.4 Char-Oxygen Reaction

Both CO and CO$_2$ are formed as the primary products of the char-oxygen reactions according to equation [8]. Thring and Essenhigh (21) studied the mechanism of this reaction and reported that the reaction rate is zero order with respect to oxygen concentration when the temperature is below 1200°K, and is first order between 1200°K and 2200°K. Field (22) suggested that for particles smaller than 50 µm the reaction rate is controlled the chemical reaction, while for larger particles (larger than 100 µm) combustion is controlled by diffusion. Mulcahy and Smith (23) reported that when the burning is at temperatures higher than 1200°K and the particles are larger than 100 µm, the reaction rate is controlled by the oxygen diffusion rate to the particle surface.

The char burning mechanism and the concentration gradients of the product gases around the char are very complicated. Wen et al. (24) discussed various models thoroughly and concluded that for large-sized particles, CO$_2$ might be the only product gas in the char-oxygen reaction while CO is the primary product if the particle size is small and the temperature is higher than 1000°K.

The mechanism factor, $\phi$, is a function of coal type, particle size, and temperature. Wen and Chaung (3) applied
a correlation proposed by Wen and Dutta (25) to estimate the mechanism factor \( \phi \) by a linear interpolation between small particles and large ones. The correlation can be represented as follows:

\[
\phi = \frac{2\cdot Z + 2}{Z + 2} \quad \text{for } d_p \leq 0.005 \text{ cm} \tag{34}
\]

\[
\phi = \frac{(2\cdot Z + 2) - \frac{Z\cdot(d_p - 0.05)}{0.095}}{Z + 2} \quad \text{for } 0.005 \text{ cm} \leq d_p \leq 0.1 \mu m \tag{35}
\]

and \( \phi = 1.0 \) \, \text{for } d_p \geq 0.1 \text{ cm} \tag{36}

where

\[
Z = \frac{\text{conc. of CO}}{\text{conc. of CO}_2} = 2500 \cdot \exp\left(-\frac{6249}{T_m}\right) \tag{37}
\]

\( d_p \) is the particle diameter in cm

and

\[
T_m = \frac{T_s + T_g}{2} \quad \text{is the mean temperature in } ^\circ \text{K} \tag{38}
\]

\( T_g \) is the gas phase temperature in \( ^\circ \text{K} \)

Field et al. (11) reported the surface reaction constant and gas film diffusion constant as:

\[
k_s = 8710 \cdot \exp\left(-\frac{17967}{T_s}\right) \tag{39}
\]

\[
k_{dg} = \frac{0.292\cdot D}{d_p \cdot T_m} \tag{40}
\]

where \( D \) is the diffusivity of oxygen in the gas film

\[
D = 4.26 \cdot \left(\frac{T_g}{1800}\right)^{1.75} \cdot \left(\frac{1}{P_t}\right) \tag{41}
\]

The effective partial pressure, \( P_1 - P_1^* \), in the overall rate equation is the partial pressure of oxygen, \( P_{O_2} \), for this reaction.
3.1.5 Char-Steam Reaction

The char-steam reaction is one of the most important reactions used industrially to produce hydrogen and carbon monoxide. The rate of this reaction has been expressed by the Langmuir-type adsorption equations in some earlier literature, while recent researchers treated it as a volumetric reaction. When the particles are smaller than 500 μm and the temperature ranges between 1000°C and 1200°C, this reaction is controlled by the chemical reaction. For the same particles at temperatures above 1200°C, the reaction is determined by the rate of diffusion through the pores in the char.

Riede and Hanesian (26) found that the graphite-steam reaction is controlled by surface reaction at temperatures between 500°C and 900°C and that the gas film diffusion gradually becomes significant when the temperature is higher than 700°C. Gray and Kimber (27) measured the surface reaction rate constant at temperatures between 2300 K and 2800 K and obtained an activation energy of 42 Kcal/mole. Based on the data of Gary and Kimber, Dobner (20) suggested a rate expression for char-steam reactions in the temperature range of an entrained-bed gasifier. The rate equation is:

\[ k_s = 247 \cdot \exp\left(-\frac{21060}{T_s}\right) \]  \[42\]

The gas film diffusion constant, \( k_{dg} \), was given by Wen and Chaung (3):
The ash layer diffusion constant, $k_{\text{ash}}$, can be estimated by equation [33].

The effective partial pressure in the overall rate equation for the char-steam reaction can be represented as:

$$P_i - P_i^* = P_{H_2O} - \frac{P_{H_2} \cdot P_{CO}}{k_{eq}}$$  \[44\]

Wen and Chaung (3) also summarized the volumetric reaction rate constant, $k_v$, for nine types of coal and char. The values of $k_v$ vary nearly three orders of magnitude at temperatures of approximately 1200°C.

Since the available kinetic data for the char-steam reaction are limited at temperatures higher than 1200°C, the accuracy of any proposed rate expression used in modelling an entrained-bed gasifier is rather difficult to estimate.

### 3.1.6 Char-Carbon Dioxide Reaction

The kinetic data concerning the char-carbon dioxide reaction are also limited. Dutta et al. (28) suggested that for particles smaller than 300 μm and at temperatures lower than 1000°C the reaction takes place almost uniformly throughout the interior of the char particle and the rate is controlled by the intrinsic chemical reaction. Yang and Steinberg (29) estimated the reaction rate between nuclear graphite and carbon dioxide at temperatures between 1200°C
and 1600°C and concluded that the rate of this reaction is controlled by both the surface reaction and diffusion. Mayers (30) proposed a rate expression, which was mentioned by Smith and Smooth (31), to calculate the surface reaction rate at temperatures between 1000°C and 1160°C. The equation is:

\[ k_s = 0.2 \cdot \exp\left(\frac{-7876}{T_s}\right) \]  \[45\]

The gas film diffusion constant is given by Wen and Chaung(3):

\[ k_{dg} = \frac{7.45 \cdot 10^{-4} \cdot \left(\frac{T_s}{2000}\right)^{0.75}}{P_t \cdot d_p} \]  \[46\]

The ash layer diffusion constant, \( k_{\text{dash}} \), can be estimated by equation [33].

The partial pressure of carbon dioxide, \( P_{CO_2} \), is taken as the effective partial pressure for the overall rate calculation.

3.1.7 Char-Hydrogen Reaction

The char-hydrogen reaction, also called the hydrogasification reaction, is very slow when the partial pressure of hydrogen and the temperature are low. The reaction rate becomes appreciable at high hydrogen partial pressure and at temperatures higher than 700°C. This is a quite exothermic reaction and its mechanism is rather complex. Several models have been reported by different researchers. Wen and
Huebler (32) proposed an empirical equation for the char-hydrogen reaction:

\[
\text{Rate} = \frac{dx}{dt} = k_v \cdot (1 - x) \cdot (P_{H_2} - \left(\frac{P_{CH_4}}{k_{eq}}\right)^{0.5}) \quad [47]
\]

where \( x = \frac{X - f}{1 - \frac{f}{4}} \) the carbon conversion in char-hydrogen reaction

\( X \): the carbon conversion at any time

\( f \): the fraction of carbon that can be converted in pyrolysis

\[
k_{eq} = 5.04 \cdot 10^{-6} \cdot \left(\frac{10222}{T_s}\right) \quad [48]
\]

Since the char-hydrogen reaction is mostly in the chemical reaction regime (\( k_s < k_{dg}, k_{dash} \)). Based on the Unreacted-Core Shrinking Model, the rate equation can be expressed as follows:

\[
\text{Rate} = k_{over} \cdot \left(\frac{6}{d_p \cdot \rho_s}\right) \cdot (P_i - P^*) \quad [49]
\]

where \( k_{over} = k_s \cdot \frac{y^2}{r^2} \)

\[
= k_s \cdot \left(\frac{r_c}{R}\right) = k_s \cdot \left(1 - x\right)^{\frac{2}{3}} \quad [50]
\]

\( x \): as defined before

and

\[
P_i - P^* = (P_{H_2} - \left(\frac{P_{CH_4}}{k_{eq}}\right)^{0.5}) \quad [51]
\]

In order to simplify the calculation procedures, Wen and Chaung (3) used an approximate conversion from \( k_v \) to \( k_s \) so that the overall rate can be estimated by the Unreacted-Core Shrinking Model. From equations [47], [49], and [50], \( k_s \) can be approximated from \( k_v \) by:
\[ k_s = k_v \cdot (1 - x)^{\frac{1}{3}} \cdot \left( \frac{\rho_s \cdot R}{3} \right) \]  \[ (52) \]

Wen and Chaung (3) suggested that the surface reaction rate constant, \( k_s \), be calculated by:

\[ k_s = 0.12 \cdot \exp \left( \frac{-17921}{T_s} \right) \]  \[ (53) \]

and the gas film diffusion constant, \( k_{dg} \), can be calculated by:

\[ k_{dg} = \frac{1.33 \cdot 10^{-3} \cdot \left( \frac{T_m}{2000} \right)^{0.75}}{d_p \cdot P_t} \]  \[ (54) \]

The ash layer diffusion constant is calculated by equation [33].

3.1.8 Water-Gas-Shift Reaction

Equation [25] was selected as the kinetic model for the water-gas-shift reaction in the FCP. The catalyst reactivity correcting factor, \( F_w \), was assumed to be 0.6.

3.1.9 Methane-Water-Reforming Reaction

Because most the operating temperatures of the experiments using the FCP were about 1150 °C, the methane-water-reforming reaction can be assumed to be first order with respect to the pressure of methane only. For the convenience in calculation, the partial pressure of methane was converted to concentration of methane, and the effect of ash was included into the rate constant, \( k \), since the mass flow rate of ash in the FCP was constant. Equation [28] can be
rate = \( F_w \cdot k \cdot C_{CH4} \) \[\text{[55]}\]

where \( k \) is the rate constant, in 1/sec

\( C_{CH4} \) is the mass flow rate of methane, g/sec

\( F_w \) is the correcting factor of the reactivity of ash

\( k = 0.5644 \cdot \exp\left(\frac{-8783.54}{1.987 \cdot T_s}\right) \) \[\text{[56]}\]

The rate is defined as the mass (g) of methane decomposed per unit time. This equation was selected for this study, with \( F_w \) chosen as 0.6, to estimate the methane-water-reforming reaction rate.

The fraction of methane decomposed in a stirred tank reactor, \( y \), can by calculated by:

\( y = 1 - \exp(-k \cdot \Delta t) \) \[\text{[57]}\]

where \( \Delta t \) is the residence time of gas in seconds.

3.1.10 Carbon Black Growth and Application of MAEROS Package

Carbon blacks can potentially undergo gasification in the third zone. However, in this study, only the particle growth process was considered.

Although the real mechanism and kinetics concerning the formation of carbon black for the FCP are still not well known, based on the experimental data, some assumptions and simplifications can be made in order to apply the MAEROS package to the calculation of average particle size of carbon blacks.

The experimental data of carbon black production are
listed in Table 4 (5, 2).

Table 4. Experimental Data of Carbon Black

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Flow Rate</td>
<td>0.38 kg/hr</td>
</tr>
<tr>
<td>Avg. Particle Size</td>
<td>200 nm</td>
</tr>
<tr>
<td>Density of Carbon Black</td>
<td>1.85 g/cm³</td>
</tr>
<tr>
<td>Isothermal Temperature</td>
<td>1370 °K</td>
</tr>
<tr>
<td>Calculated Residence Time</td>
<td>1.4 sec.</td>
</tr>
</tbody>
</table>

Based on the mass flow rate of carbon black and the calculated residence time, a certain mass of carbon black particles was considered initially to be suspended in the gas phase within a certain volume (the volume of the gasifier). Several other assumptions of initial conditions are:

(1). The initial mass concentration of carbon black was obtained by dividing the mass by the reactor volume.

(2). The initial size of each particle was given as the size of one single carbon molecule which is 2.76 nm.

(3). Because the MAEROS package does not calculate the gas-to-particle process, the coagulation between particles was assumed to be the only growth process of carbon black.
(4). The temperature of 800°K, the lowest temperature at which the coagulation process still proceeds, was assumed to be TGAS1 for the system. The isothermal temperature was taken as TGAS2, the highest temperature for the system.

(5). The largest particle size at the end of the reaction was assumed to be 750 nm so that the calculated particle range adequately covers the experimentally determined mean particle size of 200 nm.

(6). The molecular weight of the carrier gas was given as the average molecular weight of the synthesis gas produced.

(7). The reaction time was assumed to be the calculated residence time, 1.4 seconds.

(8). The atmospheric pressure was assumed to be PGAS2, the highest pressure for the system. PGAS1, the lowest pressure for the system is assumed to be 1% less than PGAS2 in order to meet the requirement of the package.

MAEROS was then applied to calculate the final particle size distribution. The mean particle size can be calculated by the following equation (33):

\[
\bar{d}_p = \frac{\int_0^\infty n_d \cdot d_p \cdot d(d_p)}{\int_0^\infty n_d \cdot d(d_p)}
\]
3.2 Hydrodynamics

One major difficulty of modelling the entrained-bed gasifier is that the degree of mixing of solid and gas flows varies along the gasifier's length and changes for each different geometry of the gasifier. Residence time data show that the combustion zone in the gasifier is similar to a stirred tank reactor, while next to the combustion zone the vortex dissipates rapidly so that plug flow with dispersion can be assumed (19).

Because of the lack of data to estimate the degree of mixing in the entrained-bed gasifier, Wen and Chaung (3) assumed that the gas phase is completely mixed at the entrance region, that the entrance region is followed by a region approximating plug flow and that solid-phase plug flow exists throughout the reactor. They also employed the compartment-in-series approach (34), which selects a large compartment size (about 1/20 of the effective reactor length) for the mixing zone immediately following the inlet and a smaller compartment size (about 1/100 of the effective reactor length) for the later compartments.

The assumptions used in this study can be summarized as follows:

(1). In the gas phase, the gases are completely mixed in the first zone, namely pyrolysis, volatile combustion and carbonization zone, followed by a region approximating plug flow
in the later sections.

(2). Compartment-in-series approach was employed.

(3). Solid phase is plug flow throughout the reactor.

(4). The gasifier is conceptually divided into three zones: the pyrolysis, volatile combustion, and carbonization zone; char, carbon black combustion and gasification zone; and char gasification, secondary gaseous reactions, and carbon black growth zone.

(5). This is a steady-state process.

3.3 Energy and Mass Balance

Based on the above assumptions, equations of energy and mass balance can be established for each compartment by referring to Figure 4.

**Gas Phase:**

\[ \Sigma(W_{g_i} \cdot C_{pgi} \cdot T_g)z + \Delta z - \Sigma(W_{g_i} \cdot C_{pgi} \cdot T_g)z = -(A_t \cdot a \cdot \Delta z) \cdot \]

\[ [\sigma \cdot F_{sg} \cdot (e_{g} \cdot T_g^4 - \alpha_g \cdot e_s \cdot T_s^4) + h_c \cdot (T_g - T_s)] + \sum(\Delta H_k) \cdot r_k \cdot A_t \cdot \]

\[ -2\pi \cdot \frac{A_t}{\pi} \cdot [\sigma \cdot F_{wg} \cdot (e_{g} \cdot T_g^4 - \alpha_g \cdot e_w \cdot T_w^4) + h_{wc} \cdot (T_g - T_w)] \]

\[ \cdot \Delta z \]

**Solid Phase:**

\[ \frac{d(W_s \cdot C_{ps} \cdot T_s)}{dz} = a \cdot A_t \cdot (\sigma \cdot F_{sg} \cdot (e_{g} \cdot T_g^4 - \alpha_g \cdot e_s \cdot T_s^4) + h_c \cdot (T_g - T_s) \]

\[ + a \cdot A_t \cdot \frac{(\Delta H_j) \cdot r_j}{(1 - \alpha_g) \cdot \sigma \cdot F_{sw} \cdot (e_s \cdot T_s^4 - e_w \cdot T_w^4)} \]

where \[ a = \frac{W_s \cdot 6}{A_t \cdot v_s \cdot \rho \cdot dp} \]
FIGURE 4. ENERGY AND MASS BALANCE IN N-TH COMPARTMENT
a is the contact area between gas and solid per unit volume of reactor (cm$^2$/cm$^3$)

$\Delta z$ is the compartment size (cm)

$W_g, W_s$ are the mass flow rate of solid and the $i$-th component gas, respectively (g/sec)

$A_t$ is the cross-sectional area of the reactor

$h_c$ is the convection and conduction heat transfer coefficient, $h_c = 2 \cdot \frac{K_g}{d_p}$ (3) [61]

$\Delta H_k, \Delta H_j$ are the reaction heats

$r_k, r_j$ are the reaction rates

$j, k$ are the reactions in solid and gas phase.

e's are the emissivities

F's are the viewing factors

By substituting the relations: $dz = v_s \cdot dt$, $e_s = 1$

$\alpha_g = e_g = e$, $F_{sg} = F$, and $H_{loss, s-w} < a \cdot A_t \cdot [\sigma \cdot F_{sg} \cdot (e_g \cdot T_g^4 - \alpha_g \cdot s \cdot T_s^4) + h_c \cdot (T_g - T_s)]$ into the above equation, the following equation is obtained:

$$\frac{dT_s}{dt} = \frac{6}{\rho_s \cdot C_{ps} \cdot d_p} \cdot [e \cdot F \cdot \sigma \cdot (T_g^4 - T_s^4) + h_c \cdot (T_g - T_s) + \sum_j (-\Delta H_j) \cdot r_j]$$ [62]

Because the FCP is an isothermal process, the calculation of gas phase temperatures can be eliminated. Equation [62] was used to solve for the solid phase temperatures.

Since the solid loading in the FCP was very small, the particles can be assumed to be surrounded by gas. Therefore the viewing factor, $F$, for radiation heat transfer between
gas and coal particles can be assumed to be 1. McAdams (35) suggested a method for an estimation of gas emissivity as the sum of $P_i L$ (atm-ft), where $P_i$ is the partial pressure of the radiating constituent and $L$ is the mean beam length. By extrapolating his data, the emissivity, $e$, was determined as 0.3 for this study.

The mass balance for the whole system was fairly easy and was done by calculating the mass flow rates of all the reactants and products according to the stoichiometric equation of each reaction involved.

The solid residence time in each compartment, $t$, can be obtained by momentum balance. Stoke's Law is assumed to be applicable in an entrained-bed gasifier because of the small particle size employed in the system. The solid entraining velocity can be calculated by the following equations:

1. Downflow:
\[
v_s = v_{si} \cdot e^{-bt} + (v_g + v_t) \cdot (1 - e^{-bt}) \quad [63]
\]
2. Upflow:
\[
v_s = v_{si} \cdot e^{-bt} + (v_g - v_t) \cdot (1 - e^{-bt}) \quad [64]
\]
where
\[
b = \frac{18 \cdot \mu}{\rho_s \cdot d_p^2} \quad [65]
\]
\[
v_t = \frac{(\rho_s - \rho_g) \cdot d_p^2 \cdot g}{18 \cdot \mu} \quad [66]
\]
\[
v_{si} = \text{initial solid velocity in cm/sec}
\]
and
\[
\Delta t = \text{solid residence in this compartment in sec.}
\]
The correlation between the residence, $\Delta t$, and the compartment size, $\Delta z$, is shown below:

$$\Delta z = \int_0^{\Delta t} v_s \, dt$$  \[67\]

Equations [63], [64], and [67] can be solved by applying the Newton-Raphson method to obtain the solid residence time, $t$, in each compartment.

The calculating procedures for the whole model can be described as follows:

1. Input the isothermal temperature as the gas phase temperature.
2. Obtain the solid temperatures from equation [62] by applying the Runge-Kutta method.
3. Do the mass balances according to the rate equations and the stoichiometric coefficients of each reaction.
4. Repeat the above three steps until the reactor length is reached.

Figure 5 shows the flowchart of the modified computer program which predicts product gas compositions. The program itself is listed in Appendix A.

Difference equations, Runge-Kutta method, and Newton-Raphson method were applied to solve the differential equations involved in the modelling mathematics. The general codes of the numerical techniques and the equations solved by them are listed in Appendix D.
FIGURE 5. COMPUTER FLOWCHART FOR THE NEW MODEL
3.4 Summary of Modifications

The original WCM is not general enough to simulate the product gas compositions of the FCP. In order for the WCM to be applicable to the FCP, some modifications were made in this study. They are summarized as follows:

(1). use a slower devolatilization rate equation.

(2). rewrite the subroutine "PYROLY".

(3). assume that the tar burn completely in the presence of oxygen, but is thermal-cracked in the absence of oxygen to form carbon black and hydrogen.

(4). adopt faster rate equations for the char-carbon dioxide reaction, the water-gas-shift reaction, and the methane-water-reforming reaction.

Detailed discussions of the above modifications are given in the next chapter. The comparisons of the different rate equations are listed in Appendix E.
CHAPTER FOUR
RESULTS AND DISCUSSIONS

4.1 The Problem of Wen and Chaung's Model

The original model developed by Wen and Chaung (3) failed to predict the experimental results of the FCP. The major reason for this failure was the error in the mass balance of oxygen. In the original computer program, a relatively high devolatilization rate was selected so that the devolatilization can be completed in the first compartment, which is the top 15 cm of the gasifier. Then this total amount of volatiles was taken into the subroutine 'PYROLY' to do the volatile combustion mass balance in order to calculate the product gas compositions at this stage. Within the PYROLY subroutine, if oxygen existed, all tar was assumed to react with the oxygen. All the tar and oxygen burned completely to become steam and carbon dioxide, no matter how much oxygen was supplied. Notice that before the PYROLY subroutine was executed, no other reaction took place except the devolatilization. Therefore, oxygen, in any case, should be existing as long as it was one of the feedstocks. For TEBPPG, the amount of oxygen in the feedstock was always more than enough to burn all the tar, methane, hydrogen, and carbon monoxide into steam and carbon dioxide. Therefore, the algorithm for volatile combustions never caused any mistake in simulating the experimental data.
of TEBPPG.

But for the FCP, the amount of oxygen supplied was not enough to burn all volatiles into steam and carbon dioxide. Thus, if all tar is assumed to become steam and carbon dioxide, an error in oxygen mass balance results. In other words, more oxygen exists in the products than in the reactants. Table 5 shows the mass balance on oxygen calculated from the computational results by WCM.

Table 5. Oxygen Mass Balance from the Computational Results of WCM for FCP

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temperature (°K)</th>
<th>O2 Input (g/sec)</th>
<th>O2 Output (g/sec)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1450</td>
<td>0.1851</td>
<td>0.3170</td>
<td>+71.3</td>
</tr>
<tr>
<td>4</td>
<td>1330</td>
<td>0.1851</td>
<td>0.3168</td>
<td>+71.2</td>
</tr>
<tr>
<td>5</td>
<td>1160</td>
<td>0.1851</td>
<td>0.3166</td>
<td>+71.0</td>
</tr>
</tbody>
</table>

O2 Input: Oxygen in Both Feedstocks and Coal
O2 Output: Oxygen in CO, CO2, and H2O

Table 6 shows the comparison between the computational results of WCM and the experimental data from the FCP. The deviation can be seen clearly.
Table 6  Comparison of Computational Results from the Original Wen & Chaung's Model with Experimental Data from Flash Carbonization Process

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temperature (K)</th>
<th>Effective Reactor Zone (cm)</th>
<th>Source</th>
<th>Dry Product Gas Mole Fraction %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H₂</td>
</tr>
<tr>
<td>3</td>
<td>1450</td>
<td>117</td>
<td>Exp.</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Original Model</td>
<td>16</td>
</tr>
<tr>
<td>4</td>
<td>1330</td>
<td>117</td>
<td>Exp.</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Original Model</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>1160</td>
<td>117</td>
<td>Exp.</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Original Model</td>
<td>14</td>
</tr>
</tbody>
</table>

Feed: Coal, 1.9 kg/hr; Oxygen, 5 liter/min; Nitrogen, 5 liter/min; Water, 2 CO/min
Pressure: 1 atm.
4.2 Modifications

In this study, some modifications were made on the volatile combustion section in the original program: first, a slower devolatilization rate was chosen in order to decrease the increment of volatile amount along the gasifier; second, the subroutine "PYROLY" was re-written so that it could take the increment of the volatiles, instead of the total amount of volatiles, as the input to do the mass balance calculations; and third, all tar was assumed to burn completely when oxygen was still present, but after the oxygen was consumed, the rest of the tar was assumed to be thermal-cracked to form carbon black and hydrogen. Table 7 shows the mass balance on oxygen calculated by the program with the above modifications.

Table 7. Oxygen Mass Balance from the Computational Results of the New Model for FCP

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temperature (°K)</th>
<th>O_2 Input (g/sec)</th>
<th>O_2 Output (g/sec)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1450</td>
<td>0.1851</td>
<td>0.1804</td>
<td>-2.5</td>
</tr>
<tr>
<td>4</td>
<td>1330</td>
<td>0.1851</td>
<td>0.1819</td>
<td>-1.7</td>
</tr>
<tr>
<td>5</td>
<td>1160</td>
<td>0.1851</td>
<td>0.1884</td>
<td>+1.8</td>
</tr>
</tbody>
</table>

O_2 Input: Oxygen in Both Feedstock and Coal
O_2 Output: Oxygen in CO, CO_2, and H_2O
Because the reactor length (330 cm) of TEBPPG is very long and the operating temperatures in TEBPPG at the early stages are very high, the reaction rates of char-gas reactions and secondary gaseous reactions do not play a very critical role in WCM. Figures 6 and 7 show the product gas compositions profiles predicted by the original WCM for two different runs of TEBPPG. It is clear to see that the gas compositions remained almost the same when the reactor length was greater than 210 cm, i.e. the whole system reached equilibrium after then. Because the FCP effective reactor lengths are short (25, 71, 117 cm) and the isothermal temperatures are lower than 1500°K, which is much lower than the early stage temperatures in TEBPPG, the reaction rates of char-gas reactions and secondary gaseous reactions become very important. Therefore, in addition to the modifications on the volatile combustion section, different reaction rate equations for the char-carbon dioxide reaction, the water-gas-shift reaction, and the methane-water reforming reaction were chosen for this study. Detailed equations were given in the previous chapter.
FIGURE 6. CALCULATED PRODUCT GAS COMPOSITION PROFILES IN TEBPPG FOR I-1 RUN, FROM WCM(3)
FIGURE 7. CALCULATED PRODUCT GAS COMPOSITION PROFILES IN TEBPPG FOR I-2 RUN, FROM WCM(3)
Another different kinetic model selected for this study was the rate of devolatilization. In WCM, in order for the devolatilization be completed within the first 15 cm of the reactor, a very high rate equation was used. Since all the volatiles produced in the devolatilization stage in TEBPPG burned completely, the accuracy of the devolatilization rate expression has no significant effect on the model's results. On the other hand, in TEBPPG, the coal liquefaction residues were used as the feed. The activity of coal residue is different from that of raw coal.

For the FCP, the experimental data show that the devolatilization was not complete if only one heating zone was applied, and was probably complete at the end of the second heating zone. Therefore, the rate of devolatilization is very important in determining the product gas compositions of those experiments with one or two heating zones. Equation [30] was satisfactory in the experimental observation, but its accuracy needs to be verified by further experiments.

4.3 Discussions on the Computational Results

Table 8 and Figures 8 to 14 show the comparison between the computational results by the new model and the experimental data of the FCP. The new model is also applicable to TEBPPG. Comparison between the computational results based on the new model and the experimental data of TEBPPG is
shown in Table 9 and Figures 15 & 16. A good agreement is still retained. In Appendix B, the temperature profiles obtained from the new model were shown and compared with those obtained from the original WCM.

For the FCP, the consideration of the second zone, namely, the char combustion and gasification zone can be eliminated due to the facts that the oxygen supply was not enough to burn all volatiles and the combustion rate of volatiles were much faster than that of char and carbon black combustions, i.e. all oxygen was consumed by volatiles before the char and carbon black combustions can take place.
### Table 8  Comparison of Computational Results from the Model Developed in this Study with Experimental Data from Flash Carbonization Process

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temperature (K)</th>
<th>Effective Reactor Zone (cm)</th>
<th>Coal Size (m)</th>
<th>Source</th>
<th>Dry Product Gas Mole Percent %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(H_2)</td>
</tr>
<tr>
<td>1</td>
<td>1450</td>
<td>25</td>
<td>250</td>
<td>Exp.</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Model</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>1450</td>
<td>71</td>
<td>250</td>
<td>Exp.</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Model</td>
<td>42</td>
</tr>
<tr>
<td>3</td>
<td>1450</td>
<td>117</td>
<td>250</td>
<td>Exp.</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Model</td>
<td>47</td>
</tr>
<tr>
<td>4</td>
<td>1330</td>
<td>117</td>
<td>250</td>
<td>Exp.</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Model</td>
<td>45</td>
</tr>
<tr>
<td>5</td>
<td>1160</td>
<td>117</td>
<td>250</td>
<td>Exp.</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Model</td>
<td>43</td>
</tr>
<tr>
<td>Run No.</td>
<td>Temperature (K)</td>
<td>Effective Reactor Zone (cm)</td>
<td>Coal Size (µm)</td>
<td>Source</td>
<td>Dry Product Gas Mole Percent %</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------</td>
<td>-----------------------------</td>
<td>----------------</td>
<td>--------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>6</td>
<td>1420</td>
<td>71</td>
<td>250</td>
<td>Exp.</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Model</td>
<td>43</td>
</tr>
<tr>
<td>7</td>
<td>1440</td>
<td>25</td>
<td>110</td>
<td>Exp.</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Model</td>
<td>38</td>
</tr>
<tr>
<td>8</td>
<td>1450</td>
<td>71</td>
<td>110</td>
<td>Exp.</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Model</td>
<td>46</td>
</tr>
<tr>
<td>9</td>
<td>1360</td>
<td>117</td>
<td>110</td>
<td>Exp.</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Model</td>
<td>49</td>
</tr>
</tbody>
</table>

Feed: Coal, 1.9 kg/hr; Oxygen, 5 liter/min; Nitrogen, 5 liter/min; Water, 2 cc/min
Pressure: 1 atm.
FIGURE 8. COMPARISON OF THE CALCULATED PRODUCT GAS COMPOSITION PROFILES WITH THE EXPERIMENTAL DATA FROM THE FCP FOR RUNS NO. 1, 2, AND 3.
Temp = 1330 K

dp = 250 um

FIGURE 9. COMPARISON OF THE CALCULATED PRODUCT GAS COMPOSITION PROFILES WITH THE EXPERIMENTAL DATA FROM THE FCP FOR RUN NO. 4
FIGURE 10. COMPARISON OF THE CALCULATED PRODUCT GAS COMPOSITION PROFILES WITH THE EXPERIMENTAL DATA FROM THE FCP FOR RUN NO. 5
FIGURE 11. COMPARISON OF THE CALCULATED PRODUCT GAS COMPOSITION PROFILES WITH THE EXPERIMENTAL DATA FROM THE FCP FOR RUN NO. 6
FIGURE 12. COMPARISON OF THE CALCULATED PRODUCT GAS COMPOSITION PROFILES WITH THE EXPERIMENTAL DATA FROM THE FCP FOR RUN NO. 7
Figure 13. Comparison of the calculated product gas composition profiles with the experimental data from the FCP for run no. 8.
FIGURE 14. COMPARISON OF THE CALCULATED PRODUCT GAS COMPOSITION PROFILES WITH THE EXPERIMENTAL DATA FROM THE FCP FOR RUN NO. 9
### Table 9  Comparison of Computational Results from the Model Developed in this Study with Experimental Data from Texaco Entrained Bed Pilot Plant Gasifier.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Fuel Rate (g/sec)</th>
<th>O₂/Fuel</th>
<th>Steam/Fuel</th>
<th>Source</th>
<th>Dry Product Gas Flow Rate (g/sec) &amp; Mole Percent</th>
<th>Carbon Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H₂, CO, CO₂, CH₄, H₂S, N₂</td>
<td></td>
</tr>
<tr>
<td>I-1</td>
<td>76.66</td>
<td>0.866</td>
<td>0.241</td>
<td>Exp.</td>
<td>6.0  123.8  10.0  0.15  0.13  0.53</td>
<td>98.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(%)</td>
<td>39.1  57.6  3.0  0.1  0.1  0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mod.</td>
<td>6.4  124.2  11.6  0.12  0.73  0.42</td>
<td>99.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(%)</td>
<td>40.4  55.7  3.3  0.3  0.3  0.2</td>
<td></td>
</tr>
<tr>
<td>I-2</td>
<td>81.18</td>
<td>0.768</td>
<td>0.314</td>
<td>Exp.</td>
<td>6.2  112.5  10.0  0.20  0.73  0.45</td>
<td>90.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(%)</td>
<td>39.8  56.6  2.9  0.2  0.3  0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mod.</td>
<td>6.4  117.2  17.1  0.09  5.68  0.43</td>
<td>92.86</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(%)</td>
<td>40.2  52.5  4.9  0.1  2.1  0.2</td>
<td></td>
</tr>
<tr>
<td>I-3</td>
<td>82.20</td>
<td>0.813</td>
<td>0.309</td>
<td>Exp.</td>
<td>6.3  121.5  19.26  0.11  0.67  0.13</td>
<td>98.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(%)</td>
<td>39.3  54.7  5.5  0.3  0.3  0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mod.</td>
<td>6.6  124.3  18.1  0.10  0.77  0.04</td>
<td>99.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(%)</td>
<td>40.1  54.3  5.0  0.1  0.3  0.2</td>
<td></td>
</tr>
<tr>
<td>I-4A</td>
<td>79.46</td>
<td>0.807</td>
<td>0.323</td>
<td>Exp.</td>
<td>5.8  116.0  16.74  0.15  0.32  0.01</td>
<td>97.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(%)</td>
<td>38.9  55.7  5.11  0.1  0.1  0.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mod.</td>
<td>6.4  117.8  19.4  0.09  0.53  0.42</td>
<td>99.78</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(%)</td>
<td>40.4  53.5  5.6  0.1  0.2  0.2</td>
<td></td>
</tr>
</tbody>
</table>
Dry Product Gas Compositions

<table>
<thead>
<tr>
<th></th>
<th>Exp.</th>
<th>Mod.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>39.1</td>
<td>40.4</td>
</tr>
<tr>
<td>CO</td>
<td>57.6</td>
<td>55.7</td>
</tr>
<tr>
<td>CO2</td>
<td>3.0</td>
<td>3.3</td>
</tr>
</tbody>
</table>

**FIGURE 15.** COMPARISON OF THE CALCULATED PRODUCT GAS COMPOSITION PROFILES WITH THE EXPERIMENTAL DATA FROM THE TEBPPG FOR I-1 RUN
FIGURE 16. COMPARISON OF THE CALCULATED PRODUCT GAS COMPOSITION PROFILES WITH THE EXPERIMENTAL DATA FROM THE TEBPPG FOR 1-2 RUN
Table 10 lists the calculated residence time and total gas yield (N2 free) of each run in the FCP.

Table 10. Calculated Residence Times and Total Gas Yields (N2 Free) for FCP

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Calc. Residence time (sec)</th>
<th>Total Gas Yield (N2 Free) (l/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3</td>
<td>551</td>
</tr>
<tr>
<td>2</td>
<td>0.8</td>
<td>798</td>
</tr>
<tr>
<td>3</td>
<td>1.4</td>
<td>1121</td>
</tr>
<tr>
<td>4</td>
<td>1.4</td>
<td>912</td>
</tr>
<tr>
<td>5</td>
<td>1.4</td>
<td>418</td>
</tr>
<tr>
<td>6</td>
<td>0.8</td>
<td>798</td>
</tr>
<tr>
<td>7</td>
<td>2.4</td>
<td>346</td>
</tr>
<tr>
<td>8</td>
<td>6.7</td>
<td>532</td>
</tr>
<tr>
<td>9</td>
<td>12.9</td>
<td>1596</td>
</tr>
</tbody>
</table>

From the above comparison, it is found that the computational results fit the experimental data better when the effective reactor length is longer and the isothermal temperature is higher. Although the exact experimental data were not predicted by the new model, the trend of the experimental data was still retained very well. The mole percents of H2 and CO increase steadily with the increase of
residence time and isothermal temperature, while the mole percent of CO₂ decreases at the same time. Poor predictions were found for runs no. 5, 7, and 8. For run no.5, the deviation was probably due to the inadequate kinetic models. As discussed in the previous chapter, the surface reactions type was applicable when temperatures are higher than 1100°C. The operating temperature for run no. 5 was only 887°C which was much lower. Instead of the surface reactions, the volumetric reactions were dominant at that temperature. Therefore, the kinetic models selected for char-gas reactions were not adequate for this run.

The reliability of the experimental data for runs no.7 and 8 is very questionable. From Table 10, the calculated residence times for these two runs are much longer than those of runs no. 1 and 2. Since the operating temperatures for these four are about the same (1440, 1450°C), runs no.7 and 8 should be able to produce more synthesis gases than runs no.1 and 2, due to the longer residence time. But the experimental data show the opposite. It was reported that, due to the mechanical difficulties in feeding finely ground coal, the experimental data for the runs with 110 μm coal particles as the feed were less reproducible (5).

In addition, several other factors influence the computational results; the first one is the compositions of volatiles. Because the oxygen supplied is consumed very fast, the shorter the reactor length is, the more the
compositions of volatiles will influence the product gas compositions. The heat transfer rate between the gas phase and coal particles is the second factor. It is very important in determining the rate of devolatilization. The heat transfer equations and the thermal conductivity of coal used in WCM were retained in this study.

4.4 Results of Particle Size Calculation

Based on the assumptions in the previous chapter concerning the application of the MAEROS package, the size distribution of carbon black is shown in Figure 17. The average particle size was calculated according to equation [58]. The result is 298 nm which is close to the experimental data of 200 nm, as measured by an electron microscope. However, attention must be paid to one possible deviation of the calculated result. The MAEROS package assumes that a spherical particle will be formed when two particles collide with each other, and calculates the particle size of the new particle. But in actuality, if the temperature is not high enough, particles will not fuse together to form a spherical particle when colliding with one another; instead, they form a long chain or a cluster. Therefore, the result calculated by the MAEROS may be larger than the actual average particle size.

The original computer output and the program that calls the MAEROS package are listed in Appendix C.
FIGURE 17. CALCULATED PARTICLE SIZE DISTRIBUTION PROFILE OF THE CARBON BLACK FROM THE FCP
4.5 **Carbon Black Formation**

The mass flow rate of carbon black calculated by the modified model was 0.51 g/sec which was only 48% of the experimental data. Two possibilities were considered: the first one is that part of the CH₄ in volatiles may undergo thermal pyrolysis or partial combustion to form carbon black according equations [14] and [15]; the second possibility is that the estimated amount of tar is too low. Both possibilities need to be verified by experiments.

4.6 **Suggestions of How to Incorporate Two Computer Programs**

The program that calls the MAEROS package can be put into the char gasification and secondary gaseous reaction section in the program that predicts the product gas compositions. When oxygen is consumed, the tar from the devolatilization is taken as the reactant of the carbon black formation reaction according to equation [2]. The initial mass concentration of the carbon black particles can be obtained by dividing the mass of carbon in the tar by the volume of the first compartment of char gasification and the secondary gaseous reaction section. The size of the carbon black particles is still assumed to be the size of one single carbon molecule. The isothermal temperature can be used as the highest temperature, TGAS2. The lowest temperature, TGAS1 can be assumed to be 5°K lower than TGAS2 in order to meet the requirement of the package. The residence
time is calculated by the "VSOLID" subroutine in the gas composition program. With the above information as the input to MAEROS, the mass concentration distribution at the end of that compartment can be obtained. Then, if devolatilization is not yet complete, this mass concentration distribution and the mass concentration from tar become the initial condition of the next compartment. By applying this algorithm, the particle mass concentration distribution at the end of the isothermal zone can be obtained.

Another extra volume and residence time should be assumed in order to let the temperature of the particles drop from the isothermal temperature to 800°K, as assumed in the previous chapter. The mass concentration at the end of this extra volume is taken as the final result.
5.1 Conclusions

(1) The model developed by Wen and Chaung has been proved to be applicable to TEBPPG only. Direct application of this model to the FCP will result in error in oxygen mass balance.

(2) Some modifications on WCM were made, including the correction of the mass balance algorithm of volatile combustions and the use of different kinetic models for devolatilization, char-carbon dioxide reaction, and methane-water-reforming reaction. The modified model is applicable to both TEBPPG and the FCP.

(3) The computational results from the new model fit the experimental data better for runs with operating temperatures higher than 1300°C and with longer effective reactor lengths. The predicted trend of the product gas compositions is consistent with the trend of the experimental data.

(4) The MAEROS package was run separately. An average carbon black particle size of 298 nm was obtained which was close to the experimental measurement of 200 nm.
5.2 Recommendations

Several fundamental but important works need to be done in the future in order to develop a complete mathematical model for the FCP. The following should be determined:

1. The true volatile compositions of the Ohio Clarion 4A coal.
2. The rate of devolatilization of the Ohio Clarion 4A coal under the operating conditions of the FCP.
3. The heat transfer rate between coal particles and carrier gases.
REFERENCES


(4) 'MAEROS User Manual', Sandia National Laboratories, Albuquerque, MN.


Leatherhead, 1967.


(33) S. K. Friedlander, Smoke, Dust and Haze, Chap. 1.


APPENDIX A

Appendix A contains: 1. the computer program developed in this study for the simulation of the FCP; 2. a sample input data file for the FCP; and 3. a sample input data file for the TEBPPG.
A-1 Computer Program

C THIS PROGRAM PREDICTS THE PRODUCT GAS COMPOSITIONS OF
C THE FLASH CARBONIZATION PROCESS

REAL KS, KDIFF, JDF, JDF2, NCFP, NCFPS, NCFPS, NCFPS, NCFPS, NCFPS, NCFPS
DIMENSION HT(20), HTUP(10), CF(10), DTHM(5), NAME(14)
DIMENSION TOS(5), FTO(14), ABL(4), TOSOL(10), FTS(5), DFTS(5), RK(15)
LOGICAL ISO
C
C ISO IS THE INDICATOR WHICH DETERMINES WHETHER THE INPUT
C DATA IS FOR ISOThermal PROCESS (FCP) OR NOT.

COMMON /SI/, FC, FD, FDY, FSTEAM, FNM1, /T0/ 1, TS, DS, DEN, CPS, PT
COMMON /S3/, TFCOAL, XMOS
COMMON /SI/, YC, YDX, YH, YM, YCR, YDR, YHR, YSR, YM
COMMON /A/, XH2, IC0, IC02, IC02, IC02, IC02, IC02, IC02, IC02, IC02, IC02, IC02
COMMON /A/, GOY, GSTEAM, SC02, SC02, SC02, SC02, SC02, SC02

DATA TISO = 140.
DATA FC = 4.92E5
DATA B = 8900.
DATA C = 0.14
DATA Q = 1.25
DATA AT = 18241.5
DATA BEDTH = 330.

READ (5,2) (MME (J), 1=1,14)
WRITE (6,2) (NAME(I), I=1,14)
READ (5,3) TA, TSTEAM, TOY, TISO, FN2
READ (5,3) YDY, YH, YM, YN
READ (5,3) YASH, XMOS, FDY, FSTEAM, TFCOAL
READ (5,4) ISO
2 FORMAT (14A4)
3 FORMAT (5F15.7)
4 FORMAT (15F15.7)
WRITE (6,1001) TA, TSTEAM, TOY, YM, YN, YASH, XMOS, FDY, FSTEAM, TFCOAL
C
C *** FC IS THE FIXED CARBON IN DMF BASIS
C *** EF IS THE ENERGIVITY
C *** USIN IS THE INLET GAS VELOCITY
C *** BEDTH IS THE REACTOR LENGTH
C *** RI AND R2 ARE THE MASS RATIOS OF CO TO CO2 AND H20 TO CO2 RESPECTIVELY
C *** PT IS THE TOTAL PRESSURE OF THE SYSTEM
C *** AT IS THE CROSS SECTIONAL AREA OF THE REACTOR
C
C IF (ISO) GO TO 5
C
C *** THE FOLLOWING DATA ARE FOR TEIACO'S PROCESS
A=4.92E5
B=8900.
C=0.14
Q=1.25
AT=18241.5
BEDTH=330.

A-1
THE FOLLOWING DATA ARE FOR THE FLASH CARBONIZATION PROCESS

A=1.8E3
B=6700.
C=0.072
Q=1.25
AT=81.0732
BEDHT=137.
FC=52.27
R1=1.25E-2
PT=1.
EF=0.3
USIN=0.223
R1=1.5
R2=2.
DENS=1.18
CPS=0.45

CPOXY=8.724
CPST=11.34
CPC02=13.83175
CPCO=8.4765
CPCH4=20.772
CPH2=7.73
CPH2S=4.77
CPN2=8.39675

FCOAL=TFCOAL'(1.-YASH)'(1.-X"OIS)

TOHUP IS CALIS D"F COAL FEED

FCOAL.TOHUP IS CAL FLON THROUGH THIS CO"PART"ENT/SEC

FCOALaSUBDNL/100 IS 6 COAL CONSU~ED

RHEAT1 IS CAL PRODUCED IN THIS CO"PART/SEC

RHEAT IS CAL 6ENERATED IN THIS CO"PART/G D"~F COAL FEED

RHEAT IS CAL SENERATED IN THIS CO"PART/SEC

F6S IS THE FRACTION OF HEAT GENERATED BY CO~H2 CO~BUSTION

F6S=0.25

SWELL=1.0
SIGMA=1.355E-12
FASH = YASH / (1 - YASH)

*** RS is the fraction of coal sulphur that does not react into gaseous product but deposited together with ash

*** RN is the fraction of coal nitrogen as defined above

RS = 0.5
YS = YS1 * (1 - RS)
YN = YN1 * (1 - RN)

IDELH = BEDHT / 20.
DELH = IDELH

*** FW6S is the fraction of heat released by water-gas-shift that is adsorbed by the solid phase

FW6S = 1.0
CALL VOLATLT(YC, YOXY, YH, YN, YS, YASH, FC, FO, FH, FN, FS, YH2, R1, R2, VMD)
VMD = VMD1 * (1 - 0.066 * ALOS(PT))
SML = SML1 * (1 - C)

YCR = YC - (VOM / 100.) * (XC02 / 28. + XC0 / 14. + XCH4 / 12. + XTAR / 12.)
YOXYR = YOXY - (VOM / 100.) * (XC02 / 44. + XCO / 28. + XH2O / 18.)
YHR = YH - (VOM / 100.) * (XH2 + XH2S / 34. + XH2O / 18. + XCH4 / 14.)
YSR = YS - (VOM / 100.) * (XH2S / 32.)
YNR = YN - (VOM / 100.) * (XN2 / 14.)

FLOXY = YOXYR / YCR
FLH = YHR / YCR
FLN = YNR / YCR
FLS = YSR / YCR
ALPHA = YCR / 12.
BETA = YHR / 1.
GAMA = YOXYR / 16.
DELTA = YNR / 14.
EPSN = YSR / 32.
WRITE(6, 547) ALPHA, BETA, GAMA, DELTA, EPSN

SML = DENS / (1 + (FASH - SML * 100.) / (1 + FASH * SML))
RP = RI1 / (SM2 + 333)
SN2IN = FN2 * TFCOAL
SOXYIN = FOXY * TFCOAL
SH20IN = (FSTEAM + XMOS) * TFCOAL

CALL HEATUP(1, TOXY, 298., HTUP, CP)
CALL HEATUP(2, TSTEAM, 298., HTUP, CP)
VAPHT = 10520.
IF (NOT. ISOTHM) VAPHT = 0.
ENTH = HTUP(1) * S0XYIN / 32. + (HTUP(2) - VAPHT) * TFCOAL * FSTEAM / 18.
CALL HEATUP(2, TA, 298., HTUP, CP)


\textbf{GH2=GH2IN} \\
\textbf{GH2S=GH2SIN} \\
\textbf{GN2=GN2IN} \\
\textbf{GCH4=GCH4IN} \\
\textbf{POXY=POXYIN} \\
\textbf{PSTEAM=PSTEAMIN} \\
\textbf{PC02=PC02IN} \\
\textbf{PCO=PCOIN} \\
\textbf{PH2=PH2IN} \\
\textbf{PH2S=PH2SIN} \\
\textbf{PN2=PN2IN} \\
\textbf{PCH4=PCH4IN} \\
\textbf{GTAR=GTARIN} \\
\textbf{K=1} \\
\textbf{TMOLE=SDXY/32.*GSTEAM/18.*GCO2/44.*GH2/2.*GHS2/34.*GNI2/28.} \\
\textbf{1.*GCH4/16.} \\
\textbf{GSUM=SDXY+GSTEAM+GCO2+GH2+GHS2+GNI2+GCH4} \\
\textbf{RHEAT1=0.} \\
\textbf{RHEAT2=0.} \\
\textbf{RHEAT3=0.} \\
\textbf{RHEAT=0.} \\
\textbf{RHT=0.} \\
\textbf{SUBDWL=0.} \\
\textbf{D2=(SML-WL)/SML} \\
\textbf{IF(D2.LE.0.08) GO TO 500} \\
\textbf{C} \\
\textbf{140 IF(TS.GT.600.) R=RP} \\
\textbf{DP=2.1R} \\
\textbf{DENS=DENS*1.1+FASH-WL/100.)/(1.+FASH)*SHELL} \\
\textbf{CALL VSOID(HLS,DENS,DP,TS,PT,AT,VIS,DENS,DELT,DUS,US)FC 02480} \\
\textbf{US=US} \\
\textbf{C} \\
\textbf{110 CONDUT=(7.7E-7)*(TS+TS)*10.75} \\
\textbf{CT=-3./(DENS*CPS*I.*CONDUT*R*SIGMA4.*T/3)*DELT} \\
\textbf{IF(ABS(CT).GT.25.) GO TO 20} \\
\textbf{ECT=EXP(CT)} \\
\textbf{GO TO 30} \\
\textbf{ECT=1.0E-12} \\
\textbf{DELT=(TS-(TS+TS)*ECT)-TS} \\
\textbf{TSM=TS+DELT/2.} \\
\textbf{TS=TS+DELT} \\
\textbf{IF(ISOTHM.AND.TS.TISO) TS=TISO} \\
\textbf{IF(ISOTHM.AND.TS.LE.1000.) TS=TISO-200.} \\
\textbf{IF(TSM.GT.1250.) TSM=1250.} \\
\textbf{C} \\
\textbf{TIME=TIME+DELT} \\
\textbf{HS=HS+DELH} \\
\textbf{AVU1=B/TS} \\
\textbf{IF(AVU1.LE.25.) GO TO 12} \\
\textbf{EAU1=0.} \\
\textbf{GO TO 13}
12  EA6U1=EXP(A6U1)
13  AK=4*EA6U1
C
    AGU2=AK*DELTIM
    IF(ABS(AGU2).LE.25.)  GO TO 15
    EA6U2=0.
    GO TO 16
15  EA6U2=EXP(A6U2)
16  DELWL=(SWL-(SWL-WL)*EA6U2)-WL
    WL=WL+DELWL
C
    WRITE(6,123) TIME,TS,WL,HS,T5,DELWL
123  FORMAT(1X,'TIME=',F15.5,' TS=',F15.5,' WL=',F15.5,' DELWL=',F15.5)
C
    DENS=DENS*(1.+FASH-WL/100.)!((1.+FASH/28.WL)
    DLW=(SWL-WL)/SWL
C
400  YCR=YCR-(DELWL/100.)*(X0012./28.+X0212./44.+XCH412./16.+STAR
     172./78.)
C
    DO 404 N=1,4
    CALL HEAT(N,T5,HT)
404  CONTINUE
C
    CALL PYROLY(SUBWL,SWL,GOXY,PXAT,GOXY,WARFP,C02P,H2SP,H2P,C0P,
     1H2P,CH4P,TARP,CSP)
C
    RHEAT1=PXAT
    GSTEAM=GSTEAM+WARFP*FCOAL
    C02=6C02+2*FCOAL
    GH2S=6GH2S+H2SP*FCOAL
    GN2=6GN2+2*FCOAL
    C0=6C0+2*FCOAL
    GH2=6GH2+2*FCOAL
    CH4=6CH4+2*FCOAL
    STAR=STAR+TARP*FCOAL
    CS=CS+CSP
    6SUM=GOXY+6STEA+6C02+6H2S+6H2+6CH4
    TMOLE=GOXY/32.+6STEA/18.+6C02/44.+6H2/2.+6CH4/18.
C
    ICARB=100.*(6C0/28.+6C02/44.+6CH4/16.+STAR/5./78.)*12./5FC0A1YC)
C
    P0XY=PT*(GOXY/32.)/TMOLE
    PSTEAM=PT*(GSTEAM/18.)/TMOLE
    PCD2=PT*(C02/44.)/TMOLE
    PCD=PT*(C0/28.)/TMOLE
    PH2=PT*(GH2/2.)/TMOLE
    PHCH4=PT*(CH4/16.)/TMOLE
    PH2S=PT*(GH2S/34.)/TMOLE
    PM2=PT*(GN2/28.)/TMOLE
C
    IF(GOXY.GT.0.)  GO TO 433
    GOXY=0.
    P0XY=0.
C
433  CALL ENTHAL(TS,TS,FCOAL,FASH,WL,CS,ENTH)
TOHUP = (ENTH - ENTHIN) / FCOAL

IF (POXYIN .GT. 0.05) GO TO 436
IF (ISOTHM) TW = TISO
HLoss = U0 * 1.4 * DT * DELH(T6 - TW)
GO TO 437

436 HLOSS = FCOAL * ABS(RHEAT1) * THL/100.
437 HTEIX = RHEAT1 - TOHUP - HLOSS / FCOAL
IF (.NOT. ISOTHM) GO TO 420
DO 411 N = 1, 8
CALL HEATUP(N, T6, 298., HTUP, CP)
411 CONTINUE
IF (G0XY .LE. 0.) GO TO 600
DO 410 N = 1, 8
CALL HEATUP(N, T6, 298., HTUP, CP)
410 CONTINUE
DELH = (HTEIX / FCOAL) / (1.003 * CP(1)/32. + STEAM * CP(2)/18. + 6CO2 * CP(3)/44. + 6CO * CP(4)/28. + 6H2S * CP(7)/34. + 6N2 * CP(8)/28.)
ERRT8 = DELH / T6

IF (.NOT. ISOTHM) GO TO 800
IF (ABS(ERRT8).LE.0.02) GO TO 800
IF (ABS(HTEIX).LE.5.0) GO TO 800
IF (ABS(DHTE).LE.0.10) GO TO 800
CALL FINDT(POXY, TISO, ITHM, T6, TSIN, DELH, HTW, T6, TBAS, IPOXY, TISO, ISOTHM)
GO TO 300

500 RHS = 0.
RHEAT2 = 0.
R = RP
DP = 2. * R
IF (WL.GE.99.95) WL = 99.95
TI = TS
DENS = DENS(1. * FASH - WL/100.)/(1. * FASH) * SWELL
Y = (1. - WL/100.)/(1. - SWELL/100.) * 0.333
RC = R*YP
CALL VSOlID(DELH, USI, TSIN, DT, PT, VIS, DENS, DELT, USI, USI)
GO TO 505

SOXY = 0.
POXY = 0.
GO TO 600

C

### WHEN OXYGEN IS STILL EXISTED, THE PARTIAL PRESSURE OF CO IS
C ALMOST ZER0 AND THE WATER-SAS-SHIFT REACTION CAN BE IGNORED
C
C 505 TSOLID(1)=TS
C
C IF(WL.GE.99.95) GO TO 560
C IF(XCARB.GE.99.75) GO TO 560
C
C Y=((1.-WL/100.)/(1.-SWL/100.))**0.333
RC=RP*Y
R=RP
DP=2.*R
CALL HEAT(1,T6,HT)
CALL HEAT(2,T6,HT)
C
C *** RUNGE-KUTTA-BILL METHOD
C
C DO 510 L=1,4
TS=TSOLID(L)
IF(ISOTH.AND.TS.GT.TISO) TS=TISO
IF(TS.LE.0.) GO TO 506
CALL COMBUS(T6,TS,PT,RP,POXY,SMW,Y,DENSP,RATE,CWL,PHI,GRH,FASH
1,DELTIM,Q1,Q2)
CALL CBSTM(DELTIM,PSTEAM,PH2,PCO,RP,PT,DENSP,T6,TS,SMW,Y,FASH
1,RATE2,CWL2,OCM,ML)
CALL CBC02(PCO2,DELTIM,ML,SMW,RP,PT,DENSP,T6,TS,SMW,Y,RATE3,CWL3,FC 04030
10CBC02)
QCCD=(RATE3/12.)*(2.*HT(2)+HT(1))*(BETA/2.-GAMA-EPSN)/ALPHA)
QCS6=(RATE2/12.)*(HT(2)+HT(1))*(ALPHA-GAMA+BETA/2.-EPSN)/ALPHA)
QCDM=(RATE/12.)*(2.-2./PHI)*HT(2)
CONDUT=(7.7E-7)*((TS+TS).**0.75)
RK(L)=(3./(DENS*CPSJR)*CONDUT*(T6-TS)/R+EF*SISMA*(T6**.4-TS**.4)
1+QRH*RATE-QCS6*RATE2/12.-QCBC02*RATE3/12.-F6S*(QCOM6+QCS6+QCCD6))
FC 04090
1+QRH*RATE=QCS6*RATE2/12.-QCBC02*RATE3/12.-F6S*(QCOM6+QCS6+QCCD6)
FC 04100
60 TO 507
506 CONDUT=(7.7E-7)*((TS)**0.75)
RK(L)=(3./(DENS*CPSJR)*CONDUT*TS/R+EF*SIGMA*(TS**4))
FC 04130
507 IF(L.EQ.1) GO TO 5071
IF(L.EQ.2) GO TO 5072
IF(L.EQ.3) GO TO 5073
IF(L.EQ.4) GO TO 510
5071 TSOLID(2)=TSOLID(1)+(DELTIM/2.)*RK(1)
GO TO 510
5072 TSOLID(3)=TSOLID(1)+0.2071*DELTIM*RK(1)+0.2929*DELTIM*RK(2)
GO TO 510
5073 TSOLID(4)=TSOLID(1)-0.7071*DELTIM*RK(2)+1.7071*DELTIM*RK(3)
GO TO 510
510 CONTINUE
TS=TSOLID(1)+(DELTIM/6.)*(RK(1)+0.58578*RK(2)+3.41422*RK(3)+RK(4))
FC 04240
IF(ISOTH.AND.TS.GT.TISO) TS=TISO
Y=((1.-WL/100.)/(1.-SWL/100.))**0.333
RC=RP*Y
CALL COMBUS(T6,TS,RP,POXY,SMW,Y,DENSP,RATE,CWL,PHI,GRH,FASH
1,DELTIM,Q1,Q2)
CALL CBSTM(DELTIM,PSTEAM,PH2,PCO,RP,PT,DENSP,T6,TS,SMW,Y,FASH
1,RATE2,CWL2,OCM,ML)
CALL CBC02(PCO2,DELTIM,ML,SMW,RP,PT,DENSP,T6,TS,SMW,Y,RATE3,CWL3,FC 04320
\[ YCR = YCR - (CWL + CWL2 + CWL3) \]
\[ ML = ML + (CWL + CWL2 + CWL3) \times 1.1 \times FLOXY + FLH + FLS + FLM \times 100. \]

### CHAR-OXYGEN REACTION

\[ \text{DOXY1} = (\text{ALPHA} + \text{BETA} / 4. - \text{EPSN} / 2. - \text{GAMA} / 2.) \times 32. \]
\[ \text{CO2P1} = \text{ALPHA} \times 44. \]
\[ \text{H2OP1} = (\text{BETA} / 2. - \text{EPSN}) \times 18. \]
\[ \text{N2P1} = (\text{DELTAL} / 2.) \times 28. \]
\[ \text{H2SP1} = \text{EPSN} \times 34. \]

### PARTIAL PRESSURE AND FLOW RATE CALCULATIONS

\[ \text{SOXYEX} = 60XY - \text{FCOAL} \times (CWL \times \text{DOXY1} + CWL2 \times \text{DOXY2} + CWL3 \times \text{DOXY3}) / (12 \times \text{ALPHA}) \]
\[ \text{IF(SOXYEX.LT.0.) GO TO 524} \]
\[ \text{60XY} = \text{SOXYEX} \]
\[ \text{COF} = 0. \]
\[ \text{GCO} = 0. \]
\[ \text{PCO} = 0. \]
\[ \text{RHTD} = 0. \]
\[ \text{GO TO 526} \]

\[ \text{60XY} = 0. \]
\[ \text{COF} = \text{ABS(60XYEX)} \times (28/16.) / \text{FCDAL} \]
\[ \text{COFMAX} = (28/12.) \times (CWL \times (12/2 - \text{PHI}) + CWL2 + CWL3) \]
\[ \text{IF(CP.F.L.E.COPTMAX) GO TO 5251} \]
\[ \text{DELYH} = \text{DELYH} / 2. \]
\[ \text{GO TO 300} \]

\[ \text{RHTD} = \text{COFHTU} \times (12/28.) \]

### CHAR-STEAM REACTION FOLLOWED BY CO AND H2(PROD) COMBUSTION

\[ \text{DOXY2} = (\text{ALPHA} + \text{BETA} / 4. - \text{GAMA} / 2. - \text{EPSN} / 2.) \times 32. \]
\[ \text{CO2P2} = \text{ALPHA} \times 44. \]
\[ \text{H2OP2} = (\text{BETA} / 2. - \text{EPSN}) \times 18. \]
\[ \text{N2P2} = (\text{DELTAL} / 2.) \times 28. \]
\[ \text{H2SP2} = \text{EPSN} \times 34. \]

### CO2 DECREASED BY ALPHA BUT INCREASED BY TWO ALPHAS

\[ \text{CO2P3} = \text{ALPHA} \times 44. \]
\[ \text{H2OP3} = (\text{BETA} / 2. - \text{EPSN}) \times 18. \]
\[ \text{N2P3} = (\text{DELTAL} / 2.) \times 28. \]
\[ \text{H2SP3} = \text{EPSN} \times 34. \]

### PARTIAL PRESSURE AND FLOW RATE CALCULATIONS

\[ \text{60XYEX} = 60XY - \text{FCOAL} \times (CWL \times \text{DOXY1} + CWL2 \times \text{DOXY2} + CWL3 \times \text{DOXY3}) / (12 \times \text{ALPHA}) \]
\[ \text{IF(SOXYEX.LT.0.) GO TO 524} \]
\[ \text{60XY} = \text{SOXYEX} \]
\[ \text{COF} = 0. \]
\[ \text{GCO} = 0. \]
\[ \text{PCO} = 0. \]
\[ \text{RHTD} = 0. \]
\[ \text{GO TO 526} \]

\[ \text{60XY} = 0. \]
\[ \text{COF} = \text{ABS(60XYEX)} \times (28/16.) / \text{FCDAL} \]
\[ \text{COFMAX} = (28/12.) \times (CWL \times (12/2 - \text{PHI}) + CWL2 + CWL3) \]
\[ \text{IF(CP.F.L.E.COPTMAX) GO TO 5251} \]
\[ \text{DELYH} = \text{DELYH} / 2. \]
\[ \text{GO TO 300} \]

\[ \text{RHTD} = \text{COFHTU} \times (12/28.) \]

### CHAR-C02 REACTION FOLLOWED BY CO COMBUSTION

\[ \text{DOXY3} = (\text{ALPHA} + \text{BETA} / 4. - \text{GAMA} / 2. - \text{EPSN} / 2.) \times 32. \]

### EQUATIONS
### Chemical Equation

\[ 6CO = 6CO + FC0AlIC0PFe04870 \]

### Total Heat of Reaction Generated in the Gas Phase

\[ \text{C Total heat of reaction generated in the gas phase}= \]

### Heat of Combustion of CO, H2 that Produced from Char-02 Reaction, Char-Steam Reaction, and Char-CO2 Reaction

\[ \text{RHTA}=\text{Q(1/12, +GRH}*\text{CWL} \]

### Heat Transfer

\[ \text{DO 1000 N=1,2} \]

\[ \text{CALL HEAT(N, TS, HT)} \]

### Heat Equation

\[ \text{RHTB}=\text{HT}(1) \text{*(ALPHA-6A"A+8ETAJ2.-EPSN)$CWL2/(ALPHA*12.)+HT(2)} \]

\[ \text{RHTC}=\text{HT}(1) \text{S(BETA/2.-6A"A-EPSN).CWL3/(12 •• ALPHA)+2 .• HT(2).CWL3/12.} \]

### Reaction, Methane Reforming Reaction

\[ \text{RHTA}=\text{Q(1/12, +GRH}*\text{CWL} \]

\[ \text{DO 1000 N=1,2} \]

\[ \text{CALL HEAT(N, TS, HT)} \]

### Heat Transfer

\[ \text{RHTB}=\text{HT}(1) \text{*(ALPHA-6A"A+8ETAJ2.-EPSN)$CWL2/(ALPHA*12.)+HT(2)} \]

\[ \text{RHTC}=\text{HT}(1) \text{S(BETA/2.-6A"A-EPSN).CWL3/(12 •• ALPHA)+2 .• HT(2).CWL3/12.} \]

### Heat Equation

\[ \text{RHEAT2}=\text{RHEAT2+RHTA+RHTB+RHTC-RHTD} \]

### Condensation

\[ \text{CONDUT}=(7.7E-7).((T6+TS)l.O.7S) \]

### Temperature

\[ \text{CT=}(-(3./(DENS.CPSIR»)I(CONDUT/R+EFlSI6"Al4.IT6113)lDELTl} \]

\[ \text{IF(ABS(CT).6T.25.) 60 TO 562} \]

\[ \text{ECT}=\text{EXP(CT)} \]

\[ \text{60 TO 564} \]

\[ \text{ECT=1.0E-12} \]

\[ \text{60 TO 564} \]

\[ \text{TS}=\text{TS}-(\text{TS}-\text{TS}')\text{ECT} \]

### Water-Gas-Shift Reaction

\[ \text{DCO}=\text{WBL} \text{FCOAL} \text{28.} \]

\[ \text{DH2O}=\text{WBL} \text{FCOAL} \text{18.} \]

\[ \text{CD2P4}=\text{WBL} \text{FCOAL} \text{44.} \]

\[ \text{H2P4}=\text{WBL} \text{FCOAL} \text{2.} \]

### Methane Reforming Reaction

\[ \text{DH2O}=\text{DCH46} \text{18./16.} \]
COPb=CDH46/16.
H2Pb=3.0CDH46/16.

RHEAT2=RHEAT2+QMREFlOCDH46/16.
RHEAT3=RHEAT3+WMSDWB.

STEAM=STEAM+DH2O4-FCOAL+CDH46.
SCO=6CD-6CD4+FCOALCDPb.
SH2=6H2+2H2P4+FCOAL2PH2P6.
SCH4=6CH4FCOAL+CDH46.
SC02=6CO2+6C02P4.

IF(STEAM.LT.0.) STEAM=0.
IF(SCO2.LE.0.) 6CO2=0.
IF(SCO.LT.0.) 6CO=0.
IF(SH2.LT.0.) 6H2=0.

SSTEAM=6STEAM+6STEA+6C02+6CO+6H2+6H2S+6N2+6CH4.

TMOLE=STEA/32.+6STEA/18.+6CD0/28.+6CO2/44.+6CO/28.+6H2/2.+6H2S/34.+6N2/28.

PT*MOL£=STEAM*(18.*TMOLE). 
PT*CO=STEAM*(28.*TMOLE).
PT*H2=STEAM*(2.*TMOLE).
PT*CH4=STEAM*(16.*TMOLE).

RHTS=0.

WHEN OXYGEN IS CONSUMED
IF(WL.6E.99.95) 60 TO 560
IF(XCARB.6E.99.75) 60 TO 560

Y=((1.-ML/100.)/(1.-SL/100.))*0.333
RC=RP*Y

RHS=0.

GO TO 700.

WHEN OXYGEN IS CONSUMED
IF(WL.6E.99.95) 60 TO 560
IF(XCARB.6E.99.75) 60 TO 560

Y=((1.-ML/100.)/(1.-SL/100.))*0.333
RC=RP*Y

RHS=0.

GO TO 700.

WHEN OXYGEN IS CONSUMED
IF(WL.6E.99.95) 60 TO 560
IF(XCARB.6E.99.75) 60 TO 560

Y=((1.-ML/100.)/(1.-SL/100.))*0.333
RC=RP*Y

RHS=0.

GO TO 700.
C *** CWL'S ARE THE GM CARBON CONSUMED PER GM DMMF COAL FOR EACH

    SPECIFIC REACTION IN EACH COMPARTMENT

C *** WGL IS THE GMOLE CONVERSION FOR WATER-GAS-SHIFT REACTION IN

    EACH COMPARTMENT PER GM DMMF COAL

C

    CONDUCT=(7.7E-7)(TS+TS)**0.75)

    RK(L)=(3./(DENS*CP)**[CONDUCT*(T6-TS)]/R+EF*SIGMA*(TS**4-TS**4]*

    1+(+G06)*RATE1*FW06-RATE2*QCSM/12.-RATE3*CBCO2/12.+(+G06H)*

    2*QSM/12.)

    IF(WL.>0.95 .AND.ABS(RK(L)).>8000.) GO TO 620

    GO TO 607

606    CONDUCT=(7.7E-7)*(TS**0.75)

607    IF(L.EQ.1) GO TO 6071

    IF(L.EQ.2) GO TO 6072

    IF(L.EQ.3) GO TO 6073

    IF(L.EQ.4) GO TO 610

6071   TSOLID(2)=TSOLID(1)+DELTIM/2.*RK(1)

6072   TSOLID(3)=TSOLID(1)+0.2071*DELTIM*RK(1)+0.2929*DELTIM*RK(2)

6073   TSOLID(4)=TSOLID(1)-0.7071*DELTIM*RK(2)+1.7071*DELTIM*RK(3)

610    CONTINUE

    TS=TSOLID(1)+((DELTIM/6.1)*(RK(1)+0.5857*RK(2)+3.4142*RK(3)+R6K(4)))

    IF(ISOTHY.AND.TS.>T6) TS=TS0

702    Y=((1.-NL/I00.)/(1.-SWL/I00.))*0.333

   RC=RP*Y

    CALL CBSTM(DELTIM,PSTEAM,PH2,PCO,RP,PT,DENS,T6,T5,Y,FASH

    1,RATE2,CWL2,QCSM,ML)

    CALL CBCO2(PCO2,DELTIM,ML,SWL,RP,PT,DENS,T6,T5,FASH,Y,FASH

    1,RCBCO2)

    CALL WSHIF(TS,PCO,PSTEAM,PCO2,PH2,RATE4,DW6,6CD,8G6,8G6,T6,8G6,8CD

    1,D6M1,F6M1,6H2)

    CALL M6SHI(FML,PCO,ML,SWL,RP,DELPNT,T6,PT)
C

COP2=ALPHA12B. Fe 06490
H2P2=(ALPHA-6AMA+BETA/2.-EPSN)12. Fe 06500
M2P2=(DELTA/2.)128. Fe 06510
H2SP2=EPSN134. FC 06520

C CHAR-CD2 REACTION
C
DCO23=ALPHA144. Fe 06550
CDP3=2.*ALPHA128. Fe 06560
H2OP3=6AMA18. Fe 06570
H2P3=(BETA/2.-GAMA-EPSN)12. Fe 06580
N2P3=(DELTA/2.)128. FC 06590
H2SP3=EPSN134. Fe 06600

C WATER-GAS-SHIFT REACTION
C
DCO4=WGL*FCOAL12B. Fe 06610
DH204=WGL*FCOAL18. Fe 06620
CD2P4=WGL*FCOAL144. Fe 06630
H2P4=WGL*FCOAL12. Fe 06640

C CHAR-HYDROGEN REACTION
C
DH2S a(2.1ALPHA+6AMA-BETA/2.)12. Fe 06650
CH4P5=ALPHA~16. Fe 06660
H2OP5=6AMA18. FC 06670
H2P5=(BETA/2.).28. FC 06680
H2SP5=EPSN134. Fe 06690

C METHANE REFORMING REACTION
C
DH206=DCH4618./16. Fe 06700
CD6P6=DCH46144. Fe 06710
H2P6=3.*DCH4612. Fe 06720

C PARTIAL PRESSURE AND FLOW RATE CALCULATIONS
C
SCH4=6CH4+FCOAL(CWL2&CH4P5)(12.*ALPHA)-FCOAL*DCH4b Fe 06730
SCH2=6CH2+FCOAL(CWL2&H2P2)(12.*ALPHA)-FCOAL*DCH2b Fe 06740
6STEA=6STEA*FCOAL(CWL3&H2P3-CWL3&H2P5+CWL5&H2P5)/(12.*ALPHA)-DC04+FCOAL.COP6
4+FCOAL*H2P6 Fe 06750

C
IF(SSTREAM.LT.0.) 6STEA=0. FC 06760
IF(DCO2.LE.0.) 6CO2=0. FC 06770

C
GLY=0. Fe 06780
POIY=0. Fe 06790

C
6CO2=6CO2+FCOAL(CWL3&H2P3-CWL2&DH2O2+H2OP5&CWl5)/(12.*ALPHA) Fe 06800
1-DH2O4-FCOAL&DC04 Fe 06810
GCO=6CO+FCOAL(CWL2&H2P2+CWL3&DC03)/(12.*ALPHA)-DC04+FCOAL*CDP6
GM2=6H2+FCOAL(CWL2&H2P2+CWL3&H2P3-CWL5&H2P3)/(12.*ALPHA)+H2P4 Fe 06820
1+FCOAL*H2P6 Fe 06830
GCH4=6CH4+FCOAL&CWl5&CH4PS/(12.*ALPHA)-FCOAL&DC04 Fe 06840
GCO2=6CO2+FCOAL&CWl3&DC023/(12.*ALPHA)+CO2P4 Fe 06850
GM2=6H2+FCOAL(CWL2&H2P2+CWL3&H2P3-CWL5&H2P5)/(12.*ALPHA) Fe 06860
GH2=6H2S+FCOAL(CWL2&H2S2+CWL3&H2S3+CWL5&H2S5)/(12.*ALPHA) Fe 06870

C
IF(SSTREAM.LT.0.) 6STEA=0. FC 06880
IF(DCO2.LE.0.) 6CO2=0. FC 06900

C
1-DH2O4-FC0AL&DC04 Fe 06910
GCO=6CO+FC0AL(CWL2&H2P2+CWL3&DC03)/(12.*ALPHA)-DC04+FC0AL*CDP6
GM2=6H2+FC0AL(CWL2&H2P2+CWL3&H2P3-CWL5&H2P3)/(12.*ALPHA)+H2P4 Fe 06920
1+FC0AL*H2P6 Fe 06930
GCH4=6CH4+FC0AL&CWl5&CH4PS/(12.*ALPHA)-FC0AL&DC04 Fe 06940
GCO2=6CO2+FC0AL&CWl3&DC023/(12.*ALPHA)+CO2P4 Fe 06950
GM2=6H2+FC0AL(CWL2&H2P2+CWL3&H2P3-CWL5&H2P5)/(12.*ALPHA) Fe 06960
GH2=6H2S+FC0AL(CWL2&H2S2+CWL3&H2S3+CWL5&H2S5)/(12.*ALPHA) Fe 06970

C
IF(SSTREAM.LT.0.) 6STEA=0. FC 06980
IF(DCO2.LE.0.) 6CO2=0. FC 06990

C
1-DH2O4-FC0AL&DC04 Fe 07000
GCO=6CO+FC0AL(CWL2&H2P2+CWL3&DC03)/(12.*ALPHA)-DC04+FC0AL*CDP6
GM2=6H2+FC0AL(CWL2&H2P2+CWL3&H2P3-CWL5&H2P3)/(12.*ALPHA) Fe 07010
GH2=6H2S+FC0AL(CWL2&H2S2+CWL3&H2S3+CWL5&H2S5)/(12.*ALPHA) Fe 07020
IF (GOI.LT.0.) GOI=0.
IF (OH2.LT.0.) OH2=0.

C
XCARB=100.*GO2/28.+GO2/44.*CH4/16.*STAR/78.*112./(FCOAL*Y)
PSTEAM=PT4*STEAM/(18.*TMOL)
PCO2=PT4*CO2/(44.*TMOL)
PCO=PT4*CO/(28.*TMOL)
FH2=PT4*H2/(2.*TMOL)
PH2S=PT4*H2S/(34.*TMOL)
PCH4=PT4*CH4/(16.*TMOL)
RHEAT2=RHEAT2+Q"REFDCH4/16.
RHEAT3=RHEAT3+QWFL*W6L/11.-FW65
RHTS=RHTS+PWS*(W6L.FW65-CW12.9*C02/12.-CW13*BC02/12.+CW15.*(-QCBHY))/12.

C
GSUM=GOY+STEAM+GO2+GO2+H2+H2S+H2+CH4

C
GOI+CH4/16.
IF (WL.GE.99.95) WL=99.95
IF (XCARB.GE.99.95) XCARB=99.95
T=TS
R=RP
DP=2.*R
DENS=DENSIAL(1.*FASH.WL/100.)/(1.*FASH.SWELL)
Y=(1.-WL/100.)/(1.-SWL/100.))**0.333
RC=RP*Y
CALL VSOLIDDELH,US1,TMOL,GSUM,DP,T,P1,AT,VS,DENS,DELT1,US1,US1
US1=US
IF (DOL.LT.0.08) TIME=TIME+DELT1
IF (DOL.LT.0.08) HS=HS+DELH

C
K=K+1
GOI+ST.0.) GOI=505
GOI=0.
POI=0.
GOI=600

C
RHEAT1=RHEAT1+RHEAT2+RHEAT3+(-RHTS)
CALL ENTHAL(TS,TS,FCOAL,FASH,WL,CPs,ENTH)
THUP=(ENTH-ENTHIH)/FCOAL

C
POI+ST.0.05) GOI=736
T=2100.-600.*HS/330.
IF (ISOTH) T=TS
HLOSS=UD*3.4*DT*DELT1*(T-G)
GOI=737
HLOSS=FCOAL*ABS*RHEAT1*WL/100.
HTEXC=-RHEAT-THUP-HLOSS/FCOAL
G
GOI=420
C
A-15

C **** CORRECTION T6 BY HALF DELT6 ****

800 IF (.NOT. ISO.THM) T6 = T6 + DELT6 /2.
IF (WL .LE. 99.99) GO TO 8010
DHS = HS - BEDHT +2.
C IF (ABS (DHS).GT.2.) GO TO 806
C IF (M .LE. 1) GO TO 806

8010 WRITE (6,801) M

801 FORMAT ('/2X,'--------- FOR GAS COMPARTMENT ',I3,' ---------')
WRITE (6,802) T6, TIME, TS, GDIY, GSTEAM, GCO2, GCO, GN2, GH2, GH2S, POXY, IPSTEAM, PCO2, PCO, PH2, PH2S, WL, BCH4, PCH4, HS

802 FORMAT ('/2X,'CORRECTED GAS TEMP = ',F9.4,'/2X,'TIME = ',E9.3,'/2X,'TS OUTLET = ',F9.4,'/2X,'OXYGEN FLOW RATE = ',F9.4,'/2X,'GM/SEC', '/2X,'G STEAM FLOW RATE = ',F9.5,'/2X,'3'S/SEC', '/2X,'CD FLOW RATE = ',F9.4,'/2X,'GM/SEC', '/2X,'N2 FLOW RATE = ',F9.4,'/2X,'SM/SEC', '/2X,'H2 FLOW RATE = ',F9.4,'/2X,'GM/SEC', '/2X,'H2S FLOW = FC 07710

5RATE = ',F9.5,'/2X,'GM/SEC', '/2X,'OXYGEN PRESSURE = ',F9.5,'/2X,'ATM', '/2X,'G STEAM PRESSURE = ',F9.5,'/2X,'ATM', '/2X,'CO2 PRESSURE = ',F9.5,'/2X,'ATM', '/2X,'CO PRESSURE = ',F9.5,'/2X,'ATM', '/2X,'N2 PRESSURE = ',F9.5,'/2X,'ATM', '/2X,'H2S PRESSURE = ',F9.5,'/2X,'ATM', FC 07720

7X,'CD PRESSURE = ',F9.5,'/2X,'ATM', '/2X,'N2 PRESSURE = ',F9.5,'/2X,'ATM', '/2X,'H2S PRESSURE = ',F9.5,'/2X,'ATM', FC 07730

9,'/2X,'TOTAL WEIGHT LOSS = ',F9.1,'/2X,'6CH4 = ',F9.1,'/2X,'PCH4 = FC 07740

= ',F9.5,'/2X,'ATM', '/2X,'BED HEIGHT = ',F9.5,'/2X,'CH')
WRITE (6,805) TAR, CS

805 FORMAT ('/2X,'TAR YIELD = ',F15.5,'/2X,'C.B. = ',F10.5)

DRYP = PT - PSTEAM
COMOL = (PCO/DRYP) *100.
C02MOL = (PCO2/DRYP) *100.
H2MOL = (PH2/DRYP) *100.
CH4MOL = (PCH4/DRYP) *100.
N2MOL = (PN2/DRYP) *100.
H2SMOL = (PH2S/DRYP) *100.
WRITE (6,862) COMOL, C02MOL, CH4MOL, N2MOL, H2SMOL

862 FORMAT ('/2X,'CO MOL % = ',F7.3,'/2X,'H2 MOL % = ',F7.3,'/2X,'CO2 MOL % = ',F7.3,'/2X,'CH4 MOL % = ',F7.3,'/2X,'N2 MOL % = ',F7.3,'/2X,'H2S MOL % = FC 07860

1 = ',F7.3,'/2X,'CH4 MOL % = ',F7.3,'/2X,'N2 MOL % = ',F7.3,'/2X,'H2S MOL % = FC 07880

2 = ',F7,3) FC 07900

IF (XCARB .GE. 99.95) XCARB = 99.95
WRITE (6,808) XCARB

808 FORMAT ('/2X,'CARBON CONVERSION = ',F10.4,'/2X,'Z')

C

C

C

806 IF (M .LE. 99.99 .AND. PDXY .GE. 0.02) GO TO 900
IF (T6 .LE. 200.) GO TO 900
IF (T6 .LE. 900.) GO TO 900
IF (M .EQ. 119) GO TO 10
C IF (HS .LE. BEDHT) GO TO 10
M = M + 1
C

C **** COMPARTMENT SIZE ADJUSTMENT ****

C DELH = 3.0
IF (US .LE. 300.) DELH = 1.75
IF (PDXY .ST. 0.01) DELH = 1.75
IF (HS .LE. 40.) DELH = 1.75
DML=(SWL-WL)/SWL
IF(DML.GT.0.08) DELH=1.75

***** RESET *****

TGIM=T6
TSIN=T5
ENTHIN=ENTH
G=1
ITERG=1
RHEAT1=0.
RHEAT2=0.
RHEAT3=0.
RHEAT=0.
SUBDNL=0.
USING=US
GOXYIN=GOXY
GH20IN=GSTEAM
BCO2IN=BCO2
GCIN=6CD
GH2IN=H2
GCH4IN=GCH4
GH2SIN=GH2S
GN2IN=SN2
PH20IN=PSTEAM
PDYIN=PDY
PC02IN=PCO2
PC0IN=P02
PH2IN=PH2
PCH4IN=PCH4
PN2IN=PN2
PH2SIN=PH2S
STARIN=STAR
TIMEIN=TIME
HSIN=HS
WLIN=WL

IF(GOXY.LE.0.) GO TO 880
TGAS(1)=TGIM+50.
TGAS(2)=TGAS(1)+100.

60 TO 890
880 TGAS(1)=TGIM-10.
TGAS(2)=TGAS(1)-10.
890 I=1
60 TO 300
900 STOP
END

SUBROUTINE VOLATL(YC, YDXY, YH, YN, YS, YASH, FC, FD, FH, FN, FS, VH2, R1, R2, I, VM2)
COMMON /A2/ XH2,XCO,XCO2,XH2S,XH20,XN2,XCH4,XTAR

*** F0, FH, FN, AND FS ARE THE % OF O2, H2, N2, AND S REMAINED IN CHAR AFTER DEVOLATILIZATION

F0=5.
FH=10.
FN=50.
FS=50.

*** VH2 IS THE AMOUNT OF H2 IN COLATILE AS % OF DMF COAL, WHICH CAN BE ESTIMATED BY LOISON-CHAUVIN CORRELATION

R1=ICD/XCO2
R2=ICD2/XH20, R1 & R2 CAN BE ESTIMATED BY LOISON-CHAUVIN CORRELATION FOR A GIVEN COAL

VH2=1.0
VH=VH2*(100.-FH)/100.
VN=VN2*(100.-FN)/100.
V5=V5*(100.-FS)/100.
V0=V0*(100.-FO)/100.

VC=VC02/VCO2
VCD2=VD/122.+(R1*16./28.)*R2*16./18.
VCD=R1*VCD2
VH2D=2*R2*VC02
VH2S=V5*24./122.
VM2=VN
H=VH-VH2-VM2*2./18.-VH2S*2./34.
C=VC-VCD*12./28.-VCD02*12./44.

VCH4=(11.2-CH4*12./16.-12./16.)/16./78.
VTAR=(H-VCH4*16./16.)/78.

VM0=VH2+VCD+VCD2+VCH4+VTAR+VM2+VH2S+VH20

XH2=VH2/VM0
ICD=VCD/VM0
XCD2=VCD2/VM0
XH2D=VH2D/VM0
XH2S=VH2S/VM0
XN2=VN2/VM0
XCH4=VCH4/VM0
XTAR=VTAR/VM0
WRITE(6,100) XH2,XCD,XCD2,XH2S,XN2,XCH4,XTAR,XH2D,VM0

100 FORMAT(/2X,'XH2 = ',E10.4,' XCD = ',E10.4,' XCD2 = ',E10.4,' XCD2 = ',E10.4,' XCD2 = ',E10.4,' XCD2 = ',E10.4,' XCD2 = ',E10.4,' XCD2 = ',E10.4,' XCD2 = ',E10.4,' XCD2 = ',E10.4,' XCD2 = ',E10.4,' XCD2 = ',E10.4,' XCD2 = ',E10.4,' XCD2 = ',E10.4,' XCD2 = ',E10.4,' XCD2 = ',E10.4,

RETURN
END

SUBROUTINE VSOLID(DELH,USI,TMOLE,BSUM,DP,PT,AT,VIS,DENS,RTIME,1,US,UE)

*** FOR UPWARD FLOW, "DIRECT"=1.0
*** FOR DOWNWARD FLOW, "DIRECT"=-1.0

DIRECT=-1.0

RETURN
END
$U_6 = \frac{\langle T \rangle_{ML} \cdot 0.82 \cdot 0.05}{\langle AT \rangle_{PT}}$

$OEN = P \cdot S \cdot U \cdot ! \cdot (T \cdot ML \cdot 0.82 \cdot 0.05)\cdot T_6$

$ACONT = \frac{18 \cdot \langle VIS \rangle}{\langle DENS \rangle \cdot \sigma_{12}}$

$UT = \frac{(OEN - DENS) \cdot 1.98 \cdot 0.01 \cdot (18 \cdot \langle VIS \rangle)}{\langle DENS \rangle \cdot \sigma_{12}}$

IF $(USI \cdot EQ \cdot 0.)$ GO TO 10

US = $U_5$ - UT $\cdot$ DIRECT

GO TO 20

TIME = DELH / US

BCONT = ACONT $\cdot$ TIME

IF (ABS(BCONT) $\leq$ 25.) GO TO 22

EB $=$ 0.

GO TO 28

EB $=$ EXP (BCONT)

FTIME = DELH / US - (USI $-$ UT $\cdot$ DIRECT) $\cdot$ TIME / ACONT

DTIME = TIME - DTIME

IF (ABS(DTIME) $\leq$ 0.02) GO TO 35

GO TO 30

RTIME = TIME

US = - DTIME

RETURN

END

SUBROUTINE HEAT (N, TEMP, HT)

DIMENSION HT (20)

DIMENSION HT29B (20), DALPHA (20), DBETA (20), DGAMA (20)

### N = 1 IS H2 COMBUSTION, N = 2 IS CO COMBUSTION, N = 3 IS CH4 COMBUSTION, AND N = 4 IS C6H6 COMBUSTION

### THE UNIT OF HT IS CAL/GMOLE

HT29(1) = -57798.

HT29(2) = -6911.6

HT29(3) = -191760.

HT29(4) = -194920.

DALPHA(1) = -2.765

DALPHA(2) = -3.28

DALPHA(3) = 5.049

DALPHA(4) = 13.351

DBETA(1) = 0.947E-3

DBETA(2) = 7.1BE-3

DBETA(3) = -9.256E-3

DBETA(4) = -9.256E-3

DGAMA(1) = 2.63BE-7

DGAMA(2) = 2.8875E-6

DGAMA(3) = 9.501E-6

DGAMA(4) = 1.293E-5

HT(N) = HT29(N) $+$ DALPHA(N) $\cdot$ (TEMP - 298.) $-$ DBETA(N) $\cdot$ (TEMP$^2$ - 298.$^2$) $+$ DGAMA(N) $\cdot$ (TEMP$^3$ - 298.$^3$) / 3.

RETURN

END
SUBROUTINE HEATUP(H,TEffP,TI,HTUP,CP)
DIMENSION HTUP(30),ALPHA(30),BETA(30),GAMA(30),CP(30)

*** N=1 IS O2, N=2 IS STEAM, N=3 IS CO2, N=4 IS CO, N=5 IS CH4, N=6 IS H2, N=7 IS H2S, AND N=8 IS N2
*** THE UNIT OF TEMP IS K AND THAT OF HTUP IS CAL/GMOLE

ALPHA(1)=6.148
ALPHA(2)=7.256
ALPHA(3)=6.214
ALPHA(4)=6.42
ALPHA(5)=3.381
ALPHA(6)=6.947
ALPHA(7)=6.662
ALPHA(8)=6.524
BETA(1)=5.102E-3
BETA(2)=2.298E-3
BETA(3)=1.0396E-2
BETA(4)=1.665E-3
BETA(5)=1.8044E-2
BETA(6)=0.2E-3
BETA(7)=5.134E-3
BETA(8)=-0.2E-3
GAMA(1)=-0.923E-6
GAMA(2)=-0.283E-6
GAMA(3)=-3.545E-6
GAMA(4)=-0.196E-6
GAMA(5)=-4.3E-6
GAMA(6)=-0.481E-6
GAMA(7)=-0.854E-6
GAMA(8)=-0.601E-6
CP(N)=ALPHA(N)+BETA(N)*TEMP+GAMA(N)*(TEMP#2)
HTUP(N)=ALPHA(N)*(TEMP-TI)+BETA(N)*(TEMP#2-TI#2)/2.
1+GAMA(N)*(TEMP#3-TI#3)/3.
RETURN
END

SUBROUTINE ENTHAl(T6,TS,FCOAL,FASH,ML,CPS,ENTH)
DIMENSION HTUP(30),ALPHA(30),BETA(30),GAMA(30),CP(30)
COMMON /A3/ GOXY,6STEAM,6CO2,6CO,6H2,6H2S,6N2,6CH4
DO 50 N=1,8
CALL HEATUP(N,Tg,298.,HTUP,CP)
50 CONTINUE
ENThS=HTUP(1)*GOXY/32.+HTUP(2)*6STEAM/18.+HTUP(3)*6CO2/44.+HTUP(4)*FC 10200
166CD/28.+HTUP(5)*6CH4/16.+HTUP(6)*6H2/2.+HTUP(7)*6H2S/34.+HTUP(8)
216N2/28.
ENThS=CP$*FCOAL*11.+FASH-ML/100.)/(TS-298.)
ENTH=ENThS+ENThS
RETURN
END
SUBROUTINE CBST(TS,TS,RP,POXY,SWL,Y,DENSP,RATE,CWL,PHI,GH
1,FASH,DELTIM,Q1,Q2)
REAL KS,KDIFF,KDASH,KOVER
DP=2.0
VOID=0.75
TM=(TS+TS)/2.
Q1=-.94051-.3.964*(TS-298,)+(3.077E-3)*(TS*TS-298.298,)
1+(8.85E-3)*(TS**3-298.298,)
Q2=-.2644+.0.847*(TS-298,)-(0.513E-3)*(TS*TS-298.298,)
1+(8.85E-3)*(TS**3-298.298,)
Z=2500.*EXP(-.6249,TM)
IF(DP.LT.5.0E-4) GO TO 10
IF(DP.LE.0.1) GO TO 20
GO TO 30
10 PHI=(Q1/12.)*(2./PHI-1.)-(Q2/12.)*(2./PHI)
GO TO 40
20 PHI=(Q1/12.)*(DP-0.005)/(Q1/12.)
GO TO 40
30 PHI=1.0
40 QRH=-(Q1/12.)*(2./PHI-1.)-(Q2/12.)*(2./PHI)
IF(PH2.LE.0.1) GO TO 55
IF(TS.LT.273.) GO TO 55
ATS=-17967./TS
IF(ABS(ATS).GT.49.) GO TO 33
EATS=EXP(ATS)
GO TO 44
33 EATS=1.0E-15
44 KS8710.*EATS
DIFF=(4.26JPT)/(TS/1800.)**1.75
KDIFF=(PHI**0.292)*DIFF)/(DP*TM)
IF(Y.EQ.0.95) GO TO 45
IF(TS.LT.273.) GO TO 45
ATS=-17967./TS
IF(ABS(ATS).GT.49.) GO TO 33
EATS=EXP(ATS)
GO TO 44
45 KOYER=1./KDASH+(1./Y)*KS
GO TO 50
50 RATE=KOVER*POXY
CWL=RATE*3.0*(1.*FASH-SWL/100.)*DELTIM/IDENSP*RP
GO TO 66
55 RATE=0.
CWL=0.
66 RETURN
END

SUBROUTINE CBSTMDELTIM,PSTEAM,PH2,PCD,RP,PT,DENSP,T6,TS,SWL,Y
1,FASH,RATE2,CWL2,QCSM,ML)
REAL KS,KDIFF,KDASH,KOVER
VOID=0.75
DP=2.0
IF(PSTEAM.LT.0.001) GO TO 10
IF(WL.LE.99.9) GO TO 10
IF(PH2.LE.0.) GO TO 5
IF(PCO.LE.0.) 60 TO 5

CTs=17.644-30260./(TS*1.8)

IF(ABS(CTs).GT.16.) 60 TO 10

CSEQK=EXP(CTs)

IF(CSEQK.GT.10000.) 60 TO 5

PEXC=PSTEAM-PH2/PCO/CSEQK

GO TO 6

5 PEXC=PSTEAM

6 IF(PEXC.LE.0.) 60 TO 10

GO TO 20

10 CWL2=0.

RATE2=0.

QCSM=0.

GO TO 30

20 TM=(TS+TB)/2.

IF(TM.LE.200.) 60 TO 10

ATS=-21080./TS

IF(ABS(ATS).GT.25.) 60 TO 10

EATS=EXP(ATS)

KS=247.*EATS

KD1FF=(10.*E-4)*(TM/2000.)**0.75/(1./PT)

IF(Y.E.0.95) 60 TO 45

KDASH=KD1FF*(VOID**2.5)

KCOVER1=1./(1./KD1FF+1./Y**Y**KS+1./KDASH)*((1./Y-1.)

GO TO 50

45 KCOVER=1./(KD1FF+1./KS)

50 RATE2=KCOVER*PEXC

CWL2=RATE2*3.**(1.+FASH-SWL/100.)*DELTM/(DENSP*RP)

QCSM=31382.+2.0111*(TS-298.)-(0.733E-3)*((TS**2-298.**2)/2.

30 RETURN
GO TO 7
6 PEXC=PH2-SQRT(PEQ)
7 IF(PEXC.LE.0.001) GO TO 10
BTS=-17921./TS
IF(ABS(BTS).GE.25.) GO TO 10
KS=0.120*EXP(BTS)
KDIFF=(1.33E-3)*(TM/2000.)^0.75/(DP*PT)
IF(Y.GE.0.95) GO TO 20
KDASH=KDIFF/(VOID**2.5)
KCOVER=1./KS
GO TO 30
20 KDASH=KDIFF/(VOID+KS)
30 RATE=KCOVER*PEXC
CWL=RATE*1.0*(1.+FASH-SML/100.)*DELTIM/(DENS*RP)
1-(S.26E-6)*(TS*TS-298.*298.)/3.
GO TO 100
10 RATE=0.
CWL=0.
QCBHY=0.
100 RETURN
END
SUBROUTINE PYROLY(WL,SWL,GOXY,HEAT,DOXY,WATERP,CO2P,H2SP,N2P,
1 COP,H2P,CH4P,CH4P,TAR,CS)
COMMON /SI/FCOAL,FOXY,FSTEAM,FN2 /SI/ TG,TS,DENS,DEN6,CPS,PT
COMMON /AI/ YC,YD,YH,YS,YN,YCR,YOXYR,YHR,YSR,YNR
COMMON /A2/ XH2,XCO,XCO2,XH2S,XH2O,XN2,XCH4,XTAR
DIMENSION HT(20)
REAL N2P
DO 402 N=1,4
CALL HEAT(N,TG,HT)
402 CONTINUE
TARP=ML*STAR/100.
CH4P=ML*CH4/100.
H2P=ML*H2/100.
CO2P=ML*CO2/100.
COF=ML*CO/100.
WATERP=ML*XH2O/100.
H2SP=ML*XH2S/100.
N2P=ML*XN2/100.
STAR=TARP*FCOAL
CH4=CH4P*FCOAL
CO2=CO2P*FCOAL
SH2=H2P*FCOAL
CO=COF*FCOAL
GN2=N2P*FCOAL
SH2S=H2SP*FCOAL
GSTEAM=WATERP*FCOAL
IF(GOXY.GT.0.) GO TO 5
TARP=0.
H2P=H2P+STAR/100.
RETURN
END
CSP=STAR/78.*72.
PHEAT=0.
GO TO 131
5 GOXY=GOXY/(32.*7.5)-STAR/78.
IF (GOXY1.6E.0.) GO TO 10
IF (GOXY1.LT.0.) GO TO 20
10 TARP=0.
CO2P=CO2P+XTAR*ML/13.*44.100.
WATERP=ML*(XH2O/18.*XTAR/26.)*18.100.
GOXY=GOXY*32.*7.5
GOXY2=GOXY/(32.*0.5)-6CO2/28.
IF (GOXY2.6E.0.) GO TO 101
IF (GOXY2.LT.0.) GO TO 102
101 CO2P=CO2P+ML*(XCO/28.)*44.100.
CO2P=0.
GOXY=GOXY*32.*10.5
GOXY3=GOXY/(32.*2.)*6CH4/16.
IF (GOXY3.6E.0.) GO TO 1011
IF (GOXY3.LT.0.) GO TO 1012
1011 CO2P=CO2P+ML*(XCH4/16.)*44.100.
WATERP=WATERP+ML*(XCH4/8.)*18.100.
CH4P=0.
GOXY=GOXY*32.*.2.
GOXY4=GOXY/(32.*0.5)-6H2/2.
IF (GOXY4.6E.0.) GO TO 200
IF (GOXY4.LT.0.) GO TO 201
200 WATERP=WATERP+ML*H2/2.18.100.
H2P=0.
GOXY=GOXY*32.*10.5
GO TO 130
201 WATERP=WATERP+GOXY/(32.*.0.5)*18./FCOAL
H2P=ABS(GOXY)*2./FCOAL
GOXY=0.
GO TO 130
1012 CO2P=CO2P+GOXY/(32.*.2.)*44./FCOAL
WATERP=WATERP+GOXY/(32.*.2.)*2.*18./FCOAL
CH4P=ABS(GOXY3)*16./FCOAL
GOXY=0.
GO TO 130
102 CO2P=CO2P+GOXY/(32.*10.5)*44./FCOAL
COP=ABS(GOXY2)*28./FCOAL
GOXY=0.
GO TO 130
20 GOXY20=GOXY/(32.*1.7343)-STAR/78.
IF (GOXY20.6T.0.) GO TO 30
TARP=0.
CSP=CSP+GOXY/(32.*1.7343)*5.5314*28./FCOAL
CO2P=CO2P+GOXY/(32.*1.7343)*0.468*44./FCOAL
WATERP=WATERP+GOXY/(32.*1.7343)*3.*18./FCOAL
H2P=H2P+ABS(GOXY20)*3.42./FCOAL
CSP=ABS(GOXY20)*72.
GOXY=0.
GO TO 130
30 TARP=0.
CDP=COP+60XY/(32.147343)*5.531428./FCOAL-SOXY202.328./FCOAL
C02P=C02P+60XY/(32.147343)*5.4686144./FCOAL+SOXY202.328./FCOAL
IF(COP.LE.0.) COP=0.
60XY=0.
GO TO 130
130 PHEAT=WL*(XH2*HT(1)/2.+XCO*HT(2)/28.+XCH4*HT(3)/16.1
*XTAR*HT(4)/78.)/100.-COP*HT(2)/28.-CH4*HT(3)/28.-H2*HT(1)/2.
131 RETURN
END

SUBROUTINE CB02(PC02,DELTI",WL,SWL,RP,PT,DENSP,T6,TS,FASH,Y
1,RATE3,CWL3,GBCDC2)
REAL KS,KDIFF,KDASH,KOVER
DP=2.*RP
VOID=0.75
IF(TS.LE.850.) 60 TO 10
IF(PC02.LE.0.) 60 TO 10
IF(WL.9E.99.9) 60 TO 100
10 CWL3=0.
RATE3=0.
GBCDC2=0.
GO TO 200
100 TM=(TS+T6)/2.
IF(TM.LE.200.) 60 TO 10
BTS=-8.4560./TS
IF(ABS(BTS).GT.25.) 60 TO 10
EBTS=EXP(BTS)
KS=2*EBTS
KDIFF=(7.45E-4)*((TM/2000.)*0.75/(DP*PT))
KDASH=KDIFF/(VOID*2.5)
IF(Y.9E.0.95) 60 TO 45
KDASH=KDASH/(VOID*2.5)
KOYER=1./(1./KDIFF+1./Y*KS)+(1./KDASH)*(-1./Y+1.))
GO TO 50
45 KOVER=1./(1./KDIFF+1./Y*KS)
50 RATE3=KOVER*PC02
CWL3=RATE3*1./(1.+FASH-SML/100.)*DELTIM/10000.*RP)
GBCDC2=41220.+2.2566*(TS-298.)/(-7.0666E-3)*(TS**2-298.**2)/2.
**+(3.153E-6)*(TS**3-298.**3)/3.
150 RETURN
END

SUBROUTINE WS6HIF(TS,PCO,PSTEAM,PC02,PH2,RATE4,QWS,BCD,6STEAM,
16CO2,GH2,DELTIM,FCOAL,FASH,WBL,TS,PT)
F=0.6
IF(TS.LE.1000.) 60 TO 10
TM=(TS+T6)/2.
CWS=EXP(-3.6893*7234./(1.8*TM))
EK=EXP(-2776.0/(1.987*TS))
EP=0.5-PT/250.
PF=PT*EP
RAT=EXP(-8.91+5553./TS)

GO TO 20

10 RATE4=0.
QWS=0.
GO TO 30

20 PEXC=PCO-PCO2*PH2/(CKW6*PSTEAM)
RATE4=FF*(2.8775)*E(1.*PEXC/PT)*FF*RAT
WGL=RATE4*DELTIM*FASH
A=1.-CKW6
B=6CO2/44.+6H2/2.+CKW6*(6CO2/28.*GSTEAM/18.)
C=(6CO2/44.)*(6H2/2.)*CKW6*(6CO2/28.)*(GSTEAM/18.)
D=B*4.*A*C
IF(D.LT.0.) 60 TO 10
IF(PEXC.LT.0.) 60 TO 25
X=(-B+SQRT(D))/(2.*A)
GO TO 26

25 X=(-B-SQRT(D))/(2.*A)

26 WGLMAX=X/FCOAL
CHECK=WGL*WGLMAX
IF(CHECK.LT.0.) 60 TO 10
IF(ABS(WGL).LT.ABS(WGLMAX)) 60 TO 27
GO TO 28

27 WGL=WGLMAX
RATE4=WGL/(DELTIM*FASH)

28 QWS=-9839.-0.5158*(TS-298.)*(6.2533E-3)*(TS**2-298.**2)/2.-(-3.151E-16)*(TS**3-298.**3)/3.
RETURN
END

SUBROUTINE CH4REF(TS,SCH4,FCDAL,DELTIM,DCH4,F,QMREF,PC4,TMOLE)

IF(TS.LE.1000.) 60 TO 10

F=0.6

EX=F*0.5644*EXP(-873.54/(1.987*TS))

DCH4=6CH4*(1.-EXP(-EX*DELTIM/TMOLE))/FCOAL

QMREF=45126.55+16.624*TS-(9.6385E-3)*TS**2+1*(1.7546E-6)*TS**3
GO TO 50

10 DCH46=0.

QMREF=0.

50 RETURN
END

SUBROUTINE FINDT(M,1,DWL,SWL,TL,ITERG,DELTG,TG1M,DELT,HTEXC

DIMENSION TESAS{4),ISOTHE)
LOGICAL ISOTHE
IF(M.EQ.1) 60 TO 302

10 DWL=(SWL-SWL)/SWL
IF(DL6.LE.0.08) GO TO 302
IF(ITER6.LE.5) GO TO 416
ITER6=ITER6+1
GO TO 302
416 DELH=DELH/2.
TGAS(1)=TGAS-30.
I=1
GO TO 300

C
C  ### WEISSTEIN METHOD
C
302 FTS(I)=TGAS(1)+DELTS
HBL(I)=HTEIC
IF(I.EQ.2) GO TO 319
IF(I.EQ.3) GO TO 339
IF(M.EQ.1) GO TO 311
TGAS(2)=TG+DELTS/2.
IF(TGAS(2).GT.4000.) TGAS(2)=TG+DELTS/5.
I=2
GO TO 300

311 TGAS(2)=TGAS(1)+100.
I=2
GO TO 300
319 CHECKS=HBL(1)*HBL(2)
IF(CHECKS.LT.0.) GO TO 322
TGAS(3)=(TGAS(1)+HBL(2)-TGAS(2)*HBL(1))/(HBL(2)-HBL(1))
I=3
GO TO 300
320 IF(POXY.LE.0.) GO TO 322
IF(ABS(HBL(1)).LE.ABS(HBL(2))) GO TO 321
TGAS(3)=TGAS(1)-(TGAS(2)-TGAS(1))
I=3
GO TO 300
321 TGAS(3)=TGAS(2)+(TGAS(1)-TGAS(2))
I=3
GO TO 300
322 TGAS(3)=(TGAS(1)-FTS(2)-TGAS(2)+FTS(1))/(TGAS(1)-TGAS(2)+FTS(2)
I-FTS(1))
I=3
GO TO 300
339 CHECK1=HBL(1)*HBL(3)
IF(CHECK1.LT.0.) GO TO 342
GO TO 340
342 TGAS(2)=TGAS(3)
FTS(2)=FTS(3)
HBL(2)=HBL(3)
GO TO 319
340 TGAS(1)=TGAS(2)
FTS(1)=FTS(2)
HBL(1)=HBL(2)
TGAS(2)=TGAS(3)
FTS(2)=FTS(3)
HBL(2)=HBL(3)
GO TO 319
SUBROUTINE MOLPCT(WL, FCOAL, COMOL, H2MOL, CO2MOL, CH4MOL, N2MOL, H2SMOL, FC 14110
1PT, PSTEAM, PCD2, PCO, PH2, PCH4, PH2S, PN2)
REAL N2MOL
DRYP = PT - PSTEAM
COMOL = PCD / DRYP * 100.
H2MOL = PH2 / DRYP * 100.
CO2MOL = PCD2 / DRYP * 100.
CH4MOL = PCH4 / DRYP * 100.
N2MOL = PN2 / DRYP * 100.
H2SMOL = PH2S / DRYP * 100.
RETURN
END
### A-2 Input File for the FCP

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APPENDIX B

Comparison of the temperature profiles and carbon conversion profiles for TEBPPG I-1 and I-2 runs calculated by WCM and the model developed in this study.
FIGURE B-1. CALCULATED TEMPERATURE PROFILES AND CARBON CONVERSION PROFILE IN TEBPPG BY THE NEW MODEL FOR I-1 RUN
FIGURE B-2. CALCULATED TEMPERATURE PROFILES AND CARBON CONVERSION PROFILE IN TEBPPG BY WCM (3) FOR I-1 RUN

FUEL RATE = 76.66 G/SEC
STEAM/FUEL = 0.241
O₂/FUEL = 0.866

© Pilot Plant Data
FIGURE B-3. CALCULATED TEMPERATURE PROFILES AND CARBON CONVERSION PROFILE IN TEBPPG BY THE NEW MODEL FOR 1-2 RUN
FUEL RATE = 81.18 G/SEC
STEAM / FUEL = 0.314
O₂ / FUEL = 0.768

FIGURE B-4. CALCULATED TEMPERATURE PROFILES AND CARBON CONVERSION PROFILE IN TEBPPG BY WCM (3) FOR I-2 RUN
APPENDIX C

The program that calls the MAEROS package and a sample output of the package are listed.
C-1 Computer Program

C THIS PROGRAM CALLS "MAEROS" PACKAGE TO CALCULATE AEROSOL
C COMPOSITION AND MASS CONCENTRATION AS A FUNCTION OF PARTICLE
C SIZE AND TIME. DEFINITIONS OF VARIABLES CAN BE FOUND IN THE
C USER'S MANUAL OF MAEROS PUBLISHED BY SANDIA NATIONAL LAB.
C THE PACKAGE ITSELF IS NOT LISTED IN THIS PROGRAM.
C
DIMENSION Q(160),SRATE(160),DEPSIT(3,3),TOUT(4),DIAM(21)
COMMON/PHYSPT/ACELOV,AFLROV,AWALOV,CHI,DELDIF,DELSAT,DENSTY,FSLIP,
$THERM,GAMMA,PSAT,STICK,TGRADC,TGRADF,TGRADM,TKSOP,TURBDS,VOLUME,
$WTCONI,WTMOL
DATA M,KCOMP,IPRT,IPLOT,ISCAL,MINW,DMINPL,GTAS1,GTAS2,GSAS1,GSAS2,
$0,1,6,6,-1.45,0.1,1.0-6,1.,800.,1370.,1.01E5,1.02E5
$/
C SET VARIABLES IN COMMON BLOCK PHYSPT
ACELOV=0.
AFLROV=0.
AWALOV=0.
CHI=1.
DELDIF=1.0E-5
DELSAT=1.0E-11
DENSTY=1.85E3
FSLIP=1.37
FTHERM=1.
GAMMA=1.
PSAT=1.01
STICK=1.
TGRAD=0.
TGRADF=0.
TGRADM=0.
TKSOP=.05
TURBDS=.001
VOLUME=0.0131
WTCONI=2.0E-26
WTMOL=16.081
C SET SECTION BOUNDARIES
DIAM(1)=2.76E-9
DIAM(M+1)=1250.0E-9
DO 2 I=2,M
2 DIAM(I)=DIAM(1)*DIAM(M+1)/DIAM(I)**(FLOAT(I-1)/FLOAT(M))
C INITIALIZE ALL SOURCES AND SECTION CONCENTRATIONS TO ZERO
MCOMP=MKCOMP
DO 4 I=1,MKCOMP
Q(I)=0.
4 SRATE(I)=0.
C DETERMINE INITIAL CONCENTRATIONS OF THE FIRST COMPONENT AND THE
C SOURCE RATE IN SECTION 1 FOR COMPONENTS 2-7
C
C ASSUME ALL THE CARBON BLACK PARTICLES INITIALLY ARE IN THE
MOLECULE SIZE RANGE SO THAT THE TOTAL MASS IS PUT INTO Q(1).
C
C IT SEEMS THAT THIS PACKAGE HAS SOME TROUBLES IF Q(2) TO Q(M) ARE
GIVEN AS ZEROS, THUS A VERY SMALL NUMBER IS ASSIGNED TO ALL THE
REST SECTIONS.
C
Q(1)=0.012
DO 1 I=2,NCOMP
Q(I)=0.0000000000000001
1 C ASSUME SRATE(SOURCE RATE) IS ZERO ALL THE TIME
C
DO 6 I=2,7
6 SRATE(I)=0.0
C
SET T6AS=T6AS1 AND P6AS=P6AS1 TO USE SECTIONAL COEFFICIENTS
AT THESE TEMPERATURES AND PressURES
C
T6AS=T6AS1
P6AS=P6AS1
TIME=0.
ROUND=9.6E-7
IFLAG=1
NEWCOF=2
DELTIM=1.4
C
CALL PRAERO Q,DEPSIT,DIA\’TIME,VOLUME,M,NCOMP,IFLAG,IPRINT,IPLOT,
$MINPL,MAIPL,ISCAL,NROW,NCOL)
C
CALL PRAERO Q,DEPSIT,DIA\’TIME,VOLUME,M,NCOMP,IFLAG,IPRINT,IPLOT,
$MINPL,MAIPL,ISCAL,NROW,NCOL)
C
STOP
END
## C-2 Sample Output from MAEROS

### TIME = 0.0 SECONDS

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TOTAL MASS CONCENTRATION
LOGARITHMICALLY SCALED Y AXIS

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0.650E-03
0.301E-03
0.144E-03
0.691E-04
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0.158E-04
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0.362E-05
0.174E-05
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0.398E-06
0.190E-06
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0.432E-07
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0.999E-08
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0.254E-09
0.126E-09
0.635E-10
0.313E-10
0.151E-11
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0.373E-12
0.174E-13
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0.912E-15
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0.408E-19
0.204E-20
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0.391E-38
0.196E-39
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0.490E-40
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**CEILING (KG)** 0.0
**VERTICAL WALLS (KG)** 0.0
**FLOOR (KG)** 0.0
**TOTAL (KG)** 0.0
**CUMULATIVE (KG)** 0.0
APPENDIX D

The general codes of three numerical methods used in solving the differential equations involved in the modelling mathematics are listed this Appendix.
Giving a first-order differential equation:

\[
\frac{dy}{dx} = f(x,y) \tag{D-1}
\]

Different numerical methods can be applied to solve the above equation:

1. By Difference Equation

Equation [D-1] can be re-written as:

\[
\Delta y = f(x,y), \text{ so that } y_{i+1} - y_i = (x_{i+1} - x_i) \cdot f(x,y) \tag{D-2}
\]

All the rate equations were solved by applying equation [D-2] in programming.

2. By Runge-Kutta Method

The Runge-Kutta method with Gill constants can be used to solve equation [D-1]. The general code of this method can be represented as:

\[
y_{i+1} = y_i + \frac{h}{6} \cdot [k_1 + 2 \cdot (1 - \frac{1}{42}) \cdot k_2 + 2 \cdot (1 + \frac{1}{42}) \cdot k_3 + k_4] \tag{D-3}
\]

where

\[
k_1 = f(x_i, y_i)
\]

\[
k_2 = f(x_i + \frac{h}{2}, y_i + \frac{h}{2})
\]

\[
k_3 = f(x_i + \frac{h}{2}, y_i + 0.20711 \cdot h \cdot k_1 + 0.29289 \cdot h \cdot k_2)
\]

\[
k_4 = f(x_i + h, y_i - 0.70711 \cdot h \cdot k_2 + 1.70711 \cdot h \cdot k_3)
\]

Equation [62] was solved by this method.
The Newton-Raphson Method can be described as follows: consider a function \( y = f(x) \) and assume \( f(x) \) has a continuous derivative \( f'(x) \), then

\[ \tan \beta = f'(x_0) = \frac{f(x_0)}{x_0 - x_1}, \]

hence

\[ x_1 = x_0 - \frac{f(x_0)}{f'(x_0)}, \]

therefore

\[ x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)} \]

The convergence criteria are

\[ |x_{n+1} - x_n| \leq \varepsilon \quad (\varepsilon > 0, \text{ given}) \]

or \[ |f(x_n)| \leq \alpha \quad (\alpha > 0, \text{ given}) \]
Appendix E contains the comparisons of the different reaction rate equations used in this study with those used in WCM.
The rate equations used for the devolatilization, the char-carbon dioxide reaction, the water-gas-shift reaction, and the methane-water-reforming reaction in this study are compared with those used in the WCM.

(1). Devolatilization

In this study:
\[
\frac{dv}{dt} = 1.8 \times 10^3 \cdot \exp\left(-\frac{13300}{1.987 \cdot T_s}\right) \cdot (V^* - V)
\]

In WCM:
\[
\frac{dv}{dt} = 1.14 \times 10^5 \cdot \exp\left(-\frac{8900}{1.987 \cdot T_s}\right) \cdot (V^* - V)
\]

(2). Char-Carbon Dioxide Reaction

In this study:
\[
k_s = 0.2 \cdot \exp\left(-\frac{7876}{T_s}\right)
\]

In WCM:
\[
k_s = 247 \cdot \exp\left(-\frac{21060}{T_s}\right)
\]

(3). Water-Gas-Shift Reaction:

The same rate equation as in the WCM was used for the water-gas-shift reaction in this study. However, the \( F_w \), the catalyst reactivity correcting factor, is 0.6 in this study but is 0.2 in WCM.
(4). Methane-Water-Reforming Reaction

In this study:

\[ \text{rate} = 0.6 \cdot k \cdot C_{\text{CH}_4} \]

\[ k = 0.5644 \cdot \exp\left(\frac{-8783.54}{1.987 \cdot T_s}\right) \]

In WCM:

\[ \text{rate} = k \cdot C_{\text{CH}_4} \]

\[ k = 312 \cdot \exp\left(\frac{-30000}{1.987 \cdot T_s}\right) \]