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**Development of Advanced Coal Devolatilization and Secondary Pyrolysis Kinetics Models
for CFD (and process simulation) Codes**

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**Thesis submitted to the
College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements**

for the degree of

Master of Science

in

Chemical Engineering

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Keywords: MFIX, PC Coal Lab, Coal Devolatilization, Secondary Pyrolysis, Soot.

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Abstract

Development of Advanced Coal Devolatilization and Secondary Pyrolysis Kinetics Models for CFD (and process simulation) Codes

Kiran Pandurang Chaudhari

Detailed kinetic expressions for the gasification of a wide variety of coals in existing Computational Fluid Dynamics (CFD) codes such as Multiphase Flow with Interphase Exchanges (MFI_X) developed by NETL. These expressions describe the fundamental steps taking place in the gasification of coal, namely, coal devolatilization, tar-gas chemistry, soot formation and the heterogeneous and homogeneous gasification reaction along with combustion reactions. For this purpose, the data generated by PC Coal Lab (PCCL) is used to simulate the gasification of various coals in CFD codes. The CFD code of most interest is MFI_X, which is used to describe the hydrodynamics, heat transfer and chemical reactions in the reacting fluid-solids systems comprising the contents of a gasifier. The implementation of gasification kinetics in MFI_X is currently done through a set of subroutines making up the Carbonaceous Chemistry for Continuum Modeling (C₃M) code. C₃M has default gasification kinetics for only a few coals. While on the other hand, PC Coal lab can predict the gasification kinetics for over 2000 coal species. This project focuses on the development of a seamless connection between PC Coal Lab and the C₃M. The interface is designed to allow MFI_X to transfer information through C₃M to PC Coal Lab, run PC Coal Lab with the input data from MFI_X, send kinetic information back to C₃M in a form that allows C₃M to update and continue the MFI_X simulation using updated parameters from PC Coal Lab. Current work is focused on developing similar expressions for biomass devolatilization. In this research PCCL predictions for biomass devolatilization were compared with experimental results and they show a good agreement with experimental results. The algorithm developed is being used to develop a Graphical User Interphase (GUI) at NETL site Morgantown by Phil Nicolletti.

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Chapter 1

Introduction

Coal is the world's most abundant and widely distributed fossil fuel source and an extremely important fuel today. Coal gasification is the method by which coal is converted to gas to generate power or processed into generating fuels or chemicals. In Gasification coal is converted into a gaseous mixture of hydrogen, carbon monoxide, carbon dioxide, methane, tar and other higher hydrocarbons by applying heat under pressure in the presence of steam and a controlled amount of oxygen in a unit called the gasifier. The standard method of describing the composition of coal is using proximate and ultimate analyses. The proximate analysis of coal gives the ash, moisture, volatile matter and fixed carbon content while the ultimate analysis gives the carbon, oxygen, hydrogen, nitrogen and sulfur content of the coal.

The gasification of coal at moderate temperatures goes through 4 stages: (1) primary devolatilization; (2) pyrolysis of secondary volatiles; (3) homogeneous reforming of non condensables and (4) char conversion via oxidation and gasification. (Naik et al., 2006) Moisture release occurs at the initial stage of reaction. Volatile matter in the coal is released as several gas phase species through devolatilization. Fixed carbon participates in combustion and gasification reactions. Ash may act as a catalyst for some gas phase reactions but it is not consumed. Devolatilization occurs at a much faster rate than gasification reactions. Many studies have been published discussing the kinetics for coal gasification.

There has been growing interest in mathematical modeling of coal processing. Different approaches have been presented to describe the gasification of coal and its behavioral changes due to varying operating conditions and process dependence on the coal's individual properties. The current research focuses on relating two such approaches. The first is that used in the software package called PC Coal Lab (PCCL) and the other is the approach currently used in the CFD package called MFIx.

1.1 Gasification Reactions

The following brief description gives an overview of the most probable reactions happening during coal gasification.

Devolatilization reaction occurs as follows:

The volatiles consist of combustible gases like CO, H₂, CH₄ and C₆H₆ together with CO₂, H₂S, N₂ and tar.

Char oxidation takes place in following manner: (Wen and Chaung, 1979)

Gasification and Combustion Reactions are represented as:

Heterogeneous reactions:

Homogeneous reactions:

Reactions other than carbon gasification may approach equilibrium in the available reaction time. Operating conditions such as heating rate, pressure, temperature and properties of coal have significant effects on the coal behavior in the gasification process. All these reactions are shown in pictorial form in Figure 1.1

The accuracy and validity of CFD models depends on the kinetic models used to describe homogeneous and heterogeneous reactions that take place in the gasifier. The homogeneous gas-phase reactions, taking place between pure components, are well known but the initial devolatilization and subsequent tar cracking reactions are less well documented especially at conditions at which the initial devolatilization takes place. Hence a good prediction of kinetics for these reactions is needed. PCCL's predictions of coal devolatilization products, tar gas chemistry and gasification reactions taking place for a wide variety of coals are in good agreement with experimental results obtained from laboratory measurements. (Niksa, 2008)

Figure 1.1 Chemical reactions in gasifier (internal DOE document)

The predictions from PCCL consist of the complete distributions of all major primary devolatilization products such as CO₂, H₂O, CO, CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈, H₂, H₂S, HCN, Tar, and Char – as well as the elemental compositions of tar and char and the tar molecular weight distribution. It also predicts the subsequent secondary pyrolysis of primary volatiles into CO₂, H₂O, CO, H₂, CH₄, C₂H₂, and soot

MFIX uses the default gasification reaction kinetics subroutines available in C₃M, which are limited to few coal types. Moreover these kinetic expressions do not give accurate predictions. Hence we need to have more accurate predictions of coal gasification kinetics and for a wider variety of coals. Therefore, the main objective of this work is to use the predicted kinetics given by PCCL and transfer these results to MFIIX by modifying the C₃M code. This work will essentially comprise of developing an algorithmic bridge which will transfer the predictions of PCCL to MFIIX by updating the relevant kinetic parameters in C₃M. The primary focus of this research will be to transfer information on kinetics for devolatilization and tar cracking reactions from PCCL to MFIIX. The process will be initiated by the user when the ultimate and proximate analysis for a coal is input in PCCL, the reaction kinetics generated from it will be transferred to C₃M in a readable form and these new values will be used in MFIIX. Hence the data transfer for the path PCCL→C₃M→ MFIIX will be implemented.

Alternatively, if the user gives the proximate and ultimate analysis for a given coal as input to MFIIX, then they should be able to run PCCL using that information and transfer the reaction kinetics to MFIIX and update the C₃M default kinetics and perform the simulation. This path would be MFIIX→PCCL→C₃M→MFIIX.

1.2 Need for a Gasification Model

One of the main reasons for developing sophisticated models for coal combustion and gasification is the different time scales that exist for the various chemical processes. For example, volatiles burn away in tens or hundreds of milliseconds, whereas char burnout requires a few seconds and char gasification requires tens of seconds. The modeling of coal reaction kinetics is both important and necessary to understanding and predicting the performance of modern gasifier (Niksa, 2008). Mathematical models help to identify key factors involved in coal

type selection, gasifier design and gasification conditions in the gasifier. Such models also save the time and cost of building and operating an experimental set up.

1.3 PC COAL LAB (PCCL)

PCCL is a set mathematical models that predicts a fuel's (mainly coal and biomass) devolatilization and gasification behavior by simulating processes as they would occur in simple laboratory test facilities. The focus of the current research is to develop a systematic method to take the results and kinetic expressions generated in PCCL Version 4.1 and use them in the C₃M code that may be called by MFIX. PCCL predicts the devolatilization, combustion, and gasification behavior of a wide variety of coals. The software can simulate two types of tests, namely, an electrically heated wire grid experiment and a laminar flow drop tube furnace experiment. The predictions give the yields of all major primary devolatilization products – CO₂, H₂O, CO, CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈, H₂, H₂S, HCN, tar, and char – as well as the elemental compositions of tar and char and the tar molecular weight distribution. It also predicts the subsequent secondary pyrolysis of primary volatiles into CO₂, H₂O, CO, H₂, CH₄, C₂H₂, and soot.

PCCL v4.1 describes char combustion from ignition throughout the later stages of burnout based on the expanded version of Hurt's Carbon Burnout Kinetics (CBK) Model (Hurt, 2002). It also describes char gasification by H₂O, CO₂, H₂, and CO with a newly expanded version of CBK called CBK/G.

In order to run PCCL, the following procedure is followed:

- a) The user selects up to five fuels for testing,
- b) Proximate and ultimate analyses are input.
- c) The method by which the simulation needs to be run is selected, either the wire grid or the drop tube method.
- d) The reactor configuration is chosen, and up to five sets of operating conditions for a particular test series are specified.
- e) Tests using the wire-grid require values for the initial and ultimate temperature, the heating rate, the reaction time at the ultimate temperature, and the pressure.

Figure 1.2: PCCL flow sheet (Niksa, 2008)

- f) Tests with the drop tube furnace require values for the initial fuel temperature, temperatures of the gas stream and reactor wall, the gas composition the pressure, mean particle size, and the total residence time.
- g) The desired results are selected and include: devolatilization behavior, the distribution of non condensable gases, the distributions of hydrocarbons with H_2 and H_2S , the N-species distributions, the O-species distributions, tar characteristics, char characteristics, and product distributions for secondary volatiles pyrolysis, char oxidation and char gasification characteristics, reaction kinetics parameters. Users select only the reports that interest them for each simulation.
- h) After entering all input information a simulation is run to attain the required results.

1.4 Multiphase Flow with Interphase Exchange (MFIx)

Currently, various CFD codes have been developed to simulate different gasifiers. The CFD code of most interest in the current study is called Multiphase Flow with Interphase Exchanges (MFIx). MFIx is a general-purpose computer code developed at The Department of Energy's National Energy Technology Laboratory (NETL) for describing the hydrodynamics, heat transfer and chemical reactions in fluid-solids systems. It has been used for describing bubbling and circulating fluidized beds and spouted beds. MFIx calculations yield transient data on the three-dimensional distribution of pressure, velocity, temperature, and species mass fractions. The MFIx code is based on a generally accepted set of multiphase flow equations. The following features of MFIx are relevant to the current work

(https://mfix.netl.doe.gov/about_mfix.php)

1. MFIx has species mass, energy and momentum balance equations for gas and solid phases.
2. It can access a 3-dimensional coordinate system with either Cartesian or cylindrical coordinates.
3. The required inputs are very simple.
4. MFIx is written in Fortran that allows users to modify easily and enhance the code.
5. MFIx generates serial, shared-memory parallel (SMP) or distributed-memory parallel (DMP) executables from the same code base.

As specified previously, MFIx simulates the reaction kinetics for coals using a default subroutine named Carbonaceous Chemistry for Continuum Modeling (C₃M). The MFIx model for coal chemistry (C₃M subroutine) is a modified version of the reaction scheme from the METC Gasifier Advanced Simulation (MGAS) (Syamlal and Bissett 1992) and is based on gasification kinetic equations proposed by Wen et al. (1982). The kinetics for coal gasification reactions other than devolatilization and tar cracking give fairly good predictions for the yield and evaluation of product gases. Figure 1.3 gives the pictorial representations of subroutines available in C₃M module.

Figure 1.3: Schematic diagram of C₃M subroutine in MFIX.

The default units used in MFIX code are grams, centimeters, seconds, calories and Kelvin.

The following table, Table 1.1, shows the one to one comparison between MFIX and PCCL regarding its functional form for gasification.

Table 1.1 Comparisons between PCCL and MFIX

Number	MFIX	PCCL
1	MGAS tracks 14 gas species, while C ₃ M module in MFIX considers only 8 it lumps all other species as tar in MFIX	PCCL gives prediction of elemental species during the whole coal gasification,

2	C ₃ M module in MFIX does not consider ash as an inert; from literature it supports that mineral content of ash can act as catalyst also for some reaction.	PCCL assumes ash to be inert.
3	For devolatilization MFIX uses the reaction kinetics available in the literature with some modified values of reaction rate constant.	PCCL uses the 3 methods to predict the devolatilization reaction kinetics namely SFOR, DAEM and C2SM methods
4	C ₃ M accounts for water gas shift reaction	PCCL does not account for water gas shift reaction
5	MFIX has first order reaction rate equation for gasification reaction.	PCCL uses simple n^{th} order rate expression for CO ₂ , H ₂ O and char hydrogen gasification reactions.
6	MFIX has different reaction kinetics for carbon, hydrogen, and tar combustion.	PCCL has char and soot combustion reaction kinetics.
7	Some gasification reaction rate equations have temperature barrier, e.g. above 1200°C the rate equation for char steam gasification reaction should not be used. Similarly Char CO ₂ reactions rate equation should be used below 1300°C	In PCCL the temperature effect is taken into consideration by the SNOR model for gasification reactions and by SFOR for devolatilization reactions.
8	Shrinking core model is used for char combustion in MFIX	PCCL does not use the shrinking core model for char combustion.

Gasification reaction rates are well studied compared to devolatilization. Devolatilization predictions given by PCCL using the FLASHCHAIN (Niksa (1991a, 1991b, 1991c, 1994b)) mechanism are more accurate when compared to laboratory data. The amount of volatiles produced and the amount of char generated will affect the subsequent gasification reactions; hence, devolatilization should be studied in detail.

Chapter 2

GASIFICATION KINETICS

In gasification, when coal is heated under pressure with steam and oxygen it gives out volatile matter, tar, and unburned char which further undergo several reactions that evolve gaseous products such as CO₂, CO, H₂O, CH₄ along with some hydrocarbons and H₂. The following sections outline a review of the reactions that take place in the gasification process and the reaction kinetics for them.

2.1 Drying

Coal consists of moisture and the evaporation of the moisture occurs during heating. When coal is heated at around atmospheric pressure uncombined water is evolved below 105°C and the remaining moisture is released when temperature approaches 300°C. (Desai and Wen, 1978)

The rate of loss of moisture from a coal is given by an equation proposed by (Syamlal and Bisset 1992):

$$\text{Rate} = 1.1 \times 10^5 \exp\left(\frac{-21,200}{RT_s}\right) \varepsilon_s \rho_s X_{s,H_2O} \quad (\text{g/cm}^3 \cdot \text{s}), \quad (2.1)$$

This rate equation is used in MFIX to calculate moisture release.

Whitty (2003) suggests the volumetric evaporation rate for a black liquor droplet as

$$m_{vap} = \frac{6h_w}{d_p \lambda_{vap}} (T_g - T_p) \quad (2.2)$$

PCCL gives the drying rate as water flux (kg/m²s) along with vapor enthalpy (J/kg) in the /output file CFDCiTj.rpt.

2.2 Devolatilization

When coal is heated to high temperatures it gives out volatiles that consist of the following component gases CO, CO₂, CH₄, H₂O, H₂, tar and higher hydrocarbons. This transformation can be simply represented as:

β and α are the respective stoichiometric coefficients for the products as mass fractions.

Devolatilization kinetics is a very complex area because of the structure variation within different types of coals. A few kinetic models treat devolatilization as a volatile release in a fractional distillation (Niksa, 1988) and others have concentrated on an analytical approach dealing with the different types of chemical bonds in a coal (Solomon, 1988). Badzioch and Hawksley (1970) proposed the devolatilization as a first order reaction with respect to volatile matter remaining in coal:

$$\text{rate} = k \exp(-E/RT) (V^* - V) \quad (2.4)$$

Some authors reported that under varying conditions like time, temperature, pressure, a first order rate equation does not hold. Ubhayakar (1977) defined two types of volatiles, benzene and ethylene that are released at different rates and this lead to the following twin reaction rate expression:

$$\text{rate} = (a_1 k_1 e^{\frac{-E_1}{RT}} + a_2 k_2 e^{\frac{-E_2}{RT}}) m_c e^{-\int (k_1 e^{\frac{-E_1}{RT}} + k_2 e^{\frac{-E_2}{RT}}) dt} \quad (2.5)$$

Where a_1 and a_2 are the possible yield of the two volatile types, m_c is mass of undevolatilised coal.

Models by Solomon (1988), van Heek (1990) and Niksa (1988) determine the rates of devolatilization of individual gases from volatile matter based on specific bond types in a coal in order to predict better accuracy. In general, more complex models are not necessary for devolatilization as this process occurs over a very short time period.

The devolatilization rate equation suggested by Wen et al. (1982) has the following simple form:

$$\text{rate} = k_d \exp(-E_d / R_g T_s) (1 - \varepsilon) \rho_s X_{VM} \quad (2.6)$$

Values of frequency factor and activation energy are given according to coal type in Table 2.1. Syamlal and Bisset (1992) modified this rate form because volatile matter release depends on temperature. The modified form of the equation used in C₃M as the devolatilization rate equation is:

$$\text{rate} = k_d \exp(-E_d / R_g T_s) (1 - \varepsilon) \rho_s (X_{VM} - X^*) ; X^* \leq X_{VM} \quad (2.7)$$

$$\text{rate} = 0 ; X_{VM} < X^* \quad (2.8)$$

Where X^* is minimum possible volatile fraction that is determined using a correlation given by Gregory and Little John (1965)

$$X_0^* = \frac{\left(\frac{867.2}{(T_s - 273)} \right)^{3.914}}{100} \quad T_s < 1223 \text{ K} \quad (2.9)$$

$$X_0^* = 0 \quad T_s > 1223 \text{ K} \quad (2.10)$$

X_0^* is the weight of remaining volatiles as a fraction of the original dry ash free coal

$$X^* = \frac{\rho_{s0}(X_{FC0} + X_{VM0})X_0^*}{\rho_s} \quad (2.11)$$

The values of k_d and E_d for different coals are given in Table 2.1

Table 2.1: Devolatilization kinetic rate constant for three types of coal

Reaction rate constant	Bituminous coal	Sub bituminous coal	Lignite
k_d [1/sec]	1.1×10^5	7.5×10^4	5.1×10^4
E_d [cal/g-mole]	21.2×10^3	18.7×10^3	16.2×10^3

Choi et al. (2001) used the following devolatilization model for an entrained flow coal gasifier;

$$m_v = m_c \left[\alpha_1 \beta_{v1} \exp\left(\frac{-E_{v1}}{RT_p}\right) + \alpha_2 \beta_{v2} \exp\left(\frac{-E_{v2}}{RT_p}\right) \right] \quad (2.12)$$

where,

E_{v1} and E_{v2} = activation energy of forward and backward reaction respectively, J/mol

β_{v1} and β_{v2} = equivalent frequency factor of forward and backward reaction, s^{-1}

α_1 = volatile constant based on combustible analysis

α_2 = empirical constant between 0.8 and 1

T_p = solid phase temperature

Chen et al. (2000) proposed the following rate equation for devolatilization in entrained flow gasifiers:

$$\frac{dY}{dt} = \frac{d(Y_1 + Y_2)}{dt} = k_1(Y_1^* - Y_1) + k_2(Y_2^* - Y_2) \quad (2.13)$$

$$k_1 = A_1 \exp(-E_1 / RT_p) \quad (2.14)$$

$$k_2 = A_2 \exp(-E_2 / RT_p) \quad (2.15)$$

Where, $A_1 = 3.7 \times 10^5 \text{ s}^{-1}$; $A_2 = 1.5 \times 10^{13} \text{ s}^{-1}$; $E_1 = 7.4 \times 10^4 \text{ kJ/mol}$; $E_2 = 2.5 \times 10^5 \text{ kJ/mol}$.

PCCL predicts the devolatilization species kinetics using the FLASHCHAIN mechanism. FLASHCHAIN represents a given coal's distinctive devolatilization behavior with very good accuracy. The FLASHCHAIN mechanism is described in detail by a series of papers by Niksa (1991a, 1991b, 1991c, 1994b)

According to this mechanism, the influences of thermal history, pressure, and particle size can be understood in terms of only four mechanisms: (1) coal macromolecules depolymerize into fragments with a broad size distribution; (2) a phase equilibrium establishes the mole fraction of tar fragments in a gas stream that are convected out of the particle with no transport resistance; (3) the conversion of labile bridges in the fragments into char links suppresses depolymerization and simultaneously generates non condensable gases; and (4) fragments also crosslink in the condensed phase to form nonvolatile components of char. However for simplicity, PCCL has only three different mechanisms to predict devolatilization such as single first-order reaction (SFOR), the competing two-step reactions model (C2SM) and the distributed activation energy model (DAEM).

The **SFOR** equation for devolatilization is

$$\frac{dV(t)}{dt} = A \exp\left(\frac{-E_a}{RT}\right) (V^\infty - V(t)) \quad (2.16)$$

where,

$V(t)$ = the instantaneous volatiles yield; % dry ash free

V^∞ = the hypothetical ultimate volatiles yield; % dry ash free

A = pseudo-frequency factor, s^{-1}

E_a = apparent activation energy, kcal/mol

A , E_a , and V^∞ are adjustable parameters that vary with temperature, heating rate, pressure, and coal type. The weight loss rate, $dV(t)/dt$, is evaluated as the sum of the total rates of tar and gas release from FLASHCHAIN. A and E_a values can be obtained in the PCCL output file called

CFDC_iT_j.rpt. The SFOR over predicts the weight loss in the initial stage of reaction with various heating rates. This is a universal flaw of SFOR.

DAEM rate equation:

The distributed activation energy model (DAEM) for devolatilization is,

$$\frac{dV(t)}{dt} = V^{\infty} \int_0^{\infty} A \exp\left(\frac{-E}{RT}\right) \exp\left[-\int_0^t A \exp\left(\frac{-E}{RT}\right) dt'\right] f(E) dE \quad (2.17)$$

where

$V(t)$ is the instantaneous volatiles yield;

V^{∞} is the hypothetical ultimate volatiles yield;

A is a pseudo-frequency factor,

E is a particular activation energy in a continuous distribution function, $f(E)$.

and

$$f(E) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(E - E_0)^2}{2\sigma^2}\right) \quad (2.18)$$

σ is the standard deviation about the mean energy.

DAEM represents the impact of temperature and heating rate variation better than SFOR and it is suited for moderate temperatures.

C2SM rate equation:

The C2SM model is discussed in detail by Kobayashi et al. (1977). The mechanism is represented as,

$$\frac{dV(t)}{dt} = \int_0^t (y_1 k_1(t') + y_2 k_2(t')) S(t') dt' \quad (2.21)$$

where

$$S = S_0 \exp\left(-\int_0^t (k_1 + k_2) dt\right) \quad (2.22)$$

S is the coal reactant; S_0 is initial coal reactant concentration;

$V_1(t)$ and $V_2(t)$ are instantaneous volatiles yields generated through channels 1 and 2, respectively;

$C_1(t)$ and $C_2(t)$ are instantaneous char yields; k_1 and k_2 are rate constants of Arrhenius form;

y_1 and y_2 are stoichiometric coefficients that are less than unity.

These six required parameters are assigned using PCCL. For simplicity the SFOR mechanism will be used when linking PCCL to MFIX.

The SFOR parameter for various operating conditions can be obtained from the output file named CFDC_iT_j.rpt under the section devolatilization parameters. PCCL generates SFOR parameters for individual species formation rate and can be obtained from the output file SFORT_iC_j.rpt.

2.3 Tar Cracking

Tar formed during the devolatilization reaction undergoes pyrolysis producing higher hydrocarbons, non condensable gases, oil, PAH and soot along with some fixed carbon.

The tar cracking rate is given by Wen et al. (1982):

Product gases consist of components lighter than C_6 , i.e., CO, CH₄, CO₂, C₂H₆, H₂O etc. The rate of tar cracking is given by,

$$\text{rate} = k_{20} \exp\left(\frac{-E_{20}}{R_g T}\right) C_{tar} \quad (2.25)$$

and tar deposits as char :

$$\text{rate} = k_{30} \exp\left(\frac{-E_{30}}{R_g T}\right) C_{tar} \quad (2.27)$$

Where k_{20} and k_{30} are rate constant, s^{-1} , E_{20} and E_{30} are activation energies (cal/mol) and C_{tar} is the concentration of tar (gmole/cm³)

Rate constant for three coal types are given in Table 2.2

Table 2.2 Tar cracking kinetic data for three coals (Wen et al. 1982)

Reaction rate constant	Bituminous coal	Sub bituminous coal	Lignite
$k_{20}(\text{sec})^{-1}$	9.7×10^9	3.5×10^{10}	8×10^{10}
$E_{20}(\text{cal/mol})$	29.0×10^3	27.75×10^3	26.50×10^3
$k_{30}(\text{sec})^{-1}$	5.3×10^4	2.5×10^4	1.1×10^3
$E_{30}(\text{cal/mol})$	7.0×10^3	5.5×10^3	4.0×10^3

Despite the problems with the simplest global rate expressions, it is always possible to identify the parameters in simple, global rate laws for tar decomposition that will match predictions closely to the predictions from the FLASHCHAI in PCCL.

The formulation follows a two-step, first-order, reaction model (Niksa, 2008)

$$\frac{d^1W_T}{dt} = {}^1R_T = {}^1k_T({}^1W_T^\infty - {}^1W_T(t)) \quad (2.28)$$

$$\frac{d\Delta W_T}{dt} = {}^2R_T = k_T(\Delta W_T^\infty - \Delta W_T(t)) \quad (2.29)$$

The first rate equation describes the release of primary tar with a conventional SFOR; and the second describes the secondary conversion of tar in terms of the difference between the instantaneous primary and secondary tar yields, i.e., $\Delta W_T = {}^1W_T(t) - W_T(t)$. Once 1W_T and ΔW_T are evaluated, $W_T(t)$ is determined as ${}^1W_T - \Delta W_T$. These data are generated by PCCL.

In PCCL, when the temperature is above 1000°C in secondary pyrolysis it is advisable to consider tar conversion into soot and if the temperature is below 1000°C the PAH are the main products of tar decomposition. Depending on availability of hydrogen, PAH may get converted into gases such as higher hydrocarbons and methane.

Rate parameters for tar decomposition can be obtained in the output file SFRT_iC_j.rpt

2.4 Secondary Pyrolysis

Primary pyrolysis (devolatilization) products include light gases, char, and tar, which is a gas mixture of heavy-molecular-weight hydrocarbons at high temperatures and condensable at room temperature. Simultaneously, the volatile matter released in the gas phase may also undergo secondary reactions. Soot is believed to be one of the products of these secondary reactions. Primary devolatilization products are transformed into secondary pyrolysis products at high temperatures such as soot, CO, CO₂, H₂O, H₂, C₂H₂ and CH₄.

Soot is made up of small carbonaceous particles. Tar, oil and PAH generated from tar cracking cannot survive high temperatures. McLean, et al. (1981) first proposed that tar is a precursor of soot in coal flames. Tar gets transformed into a soot aerosol that grows and coalesces into sooty chain agglomerates similar to soot formed in gaseous hydrocarbon flames. At moderate temperatures, PAH like tars will survive but at temperatures above 900 - 1000°C, PAH re-polymerize with non condensable unsaturated hydrocarbons to form soot (Niksa, 2008). A global mechanism for soot formation that was proposed by Chen et al. (1992) is shown below:

All reaction pathways shown above are irreversible. In the earlier stages, R_2 is the major pathway for soot formation, and nitrogen-containing compounds are incorporated in soot. Thereafter, substantial soot mass is added via R_3 . Direct tar addition to soot in later stages is possible only if tars eliminate their nitrogen before getting added to the soot. Secondary pyrolysis occurs in the gas phase; hence it can also be affected by reactive gases, especially H₂, steam, and O₂. H₂ shifts tar conversion from PAH and soot into BTX and non-condensable gaseous hydrocarbons while steam and O₂ accelerate the rate of secondary pyrolysis.

Ruiz et al. (2007) studied the influence of temperature on the properties of soot formed from C₂H₂ pyrolysis. No soot was observed at low temperatures (< 1000 °C). However, with

increase in temperature an increase of acetylene (C_2H_2) conversion into soot and H_2 was observed (Fletcher et al. 1997).

Currently the C_3M module does not include a secondary pyrolysis stage. This reaction kinetics in MFIX is introduced by adding soot and C_2H_2 as the new gas species. PCCL generates secondary pyrolysis yields for the given operating condition in the output file called FDC_iSP_j.rpt. The output file consists of secondary pyrolysis product yields on a % daf (dry-ash-free) basis. Figure 2.1 shows the output file for secondary pyrolysis of PRB coal at 1325 °C.

DROP TUBE SIMULATION WITH PC COAL LAB

FULL DYNAMICS

COAL CHARACTERISTICS: PRBCOAL

Ultimate, daf wt.% %C 75.2 %H 4.6 %O 20.2 %N 0.0 %S 0.0	Proximate, as rec wt.% Moisture 22.3 Vol. Mat. 32.9 Ash 4.6 Fixed C 40.2
--	--

OPERATING CONDITIONS:

100.0 micron particles at 25. C are entrained in N2
 with 0.0 % O2 at 1325. C in a furnace at 1325. C
 for .102E+01 s. The ambient pressure is 1.50 MPa.

Thermal History	wt.Loss	Secondary Pyrolysis Products, daf wt.%									
Time,s	Tmp,C	daf wt.%	Soot	CH4	C2H2	H2	CO	CO2	H2O	HCN	H2S
.000E+00	25.	0.0	0.0	0.0	0.0	0.00	0.0	0.0	0.0	0.00	0.0
.177E-02	78.	0.0	0.0	0.0	0.0	0.00	0.0	0.0	0.0	0.00	0.0
.398E-02	156.	0.2	0.0	0.0	0.0	0.01	0.0	0.1	0.1	0.00	0.0
.619E-02	245.	0.8	0.1	0.0	0.1	0.02	0.1	0.2	0.2	0.00	0.0
.839E-02	473.	5.9	1.7	0.1	0.1	0.25	1.2	1.3	1.2	0.00	0.0
.106E-01	682.	21.6	9.1	0.2	0.0	1.07	4.0	3.7	3.5	0.00	0.0
.128E-01	898.	40.4	16.5	0.3	0.0	1.97	7.9	7.1	6.6	0.00	0.0
.150E-01	1102.	47.8	18.9	0.4	0.1	2.36	9.8	8.4	7.8	0.00	0.0
.172E-01	1232.	49.8	19.2	0.4	0.2	2.62	10.6	8.7	8.1	0.00	0.0
.194E-01	1290.	50.7	19.3	0.4	0.3	2.90	11.0	8.7	8.1	0.00	0.0
.216E-01	1312.	51.1	19.3	0.4	0.3	3.15	11.2	8.7	8.1	0.00	0.0
.238E-01	1320.	51.3	19.3	0.4	0.3	3.18	11.4	8.7	8.1	0.00	0.0
.259E-01	1323.	51.4	19.3	0.4	0.3	3.18	11.5	8.7	8.1	0.00	0.0
.522E-01	1323.	51.5	19.3	0.4	0.3	3.18	11.6	8.7	8.1	0.00	0.0
.844E-01	1323.	51.5	19.3	0.4	0.3	3.18	11.6	8.7	8.1	0.00	0.0
.124E+00	1323.	51.5	19.3	0.4	0.3	3.18	11.6	8.7	8.1	0.00	0.0
.173E+00	1323.	51.6	19.3	0.4	0.3	3.18	11.6	8.7	8.1	0.00	0.0
.396E+00	1323.	51.6	19.3	0.4	0.3	3.18	11.6	8.7	8.1	0.00	0.0
.811E+00	1323.	51.6	19.3	0.4	0.3	3.18	11.6	8.7	8.1	0.00	0.0
.102E+01	1323.	51.6	19.3	0.4	0.3	3.18	11.6	8.7	8.1	0.00	0.0

Figure 2.1: FDC_iSP_j.rpt file showing secondary pyrolysis yields for PRB coal.

PCCL predicts soot formation based on the mechanism described by Chen et al. (1992).

The current version of PCCL is not programmed to generate soot formation kinetics. Due to this limitation, no specific kinetics are available from PCCL for soot generation.

In this research, we have lumped secondary pyrolysis and devolatilization together as a single devolatilization step. It has been assumed that secondary pyrolysis occurs only above 1000 °C so that when the reactor temperature is above 1000 °C the modified devolatilization reaction equation becomes,

This equation satisfies the mass balance. Stoichiometric coefficients are obtained from the ultimate yield predicted by PCCL. Soot formation is expressed using SFOR kinetics for devolatilization.

2.5 Combustion and Gasification Reactions

Char combustion reaction kinetics are proposed using the shrinking core model (Doraiswamy, 1986) in C₃M module of MFIX. Reaction kinetics for other gasification reactions is well established and given in the C₃M module. The predictions using this kinetics model compare well with the experimental data. Hence these gasification and combustion reaction kinetics will not be changed in MFIX during this research.

2.6 Soot Oxidation

Soot is generated via secondary pyrolysis but it can react simultaneously with steam, O₂, CO₂, and H₂. Above 800 °C soot formation competes with oxidation (Stanmore et al., 2001). The soot reactivity is directly related to its structure and composition. Properties such as surface area, particle size, and crystallinity affect the reactivity of the soot particles. The soot nanostructure depends upon its formation conditions, like fuel identity, residence time, and temperature (Ruiz et al. 2007).

This research focuses only on soot oxidation. The oxidation of soot aerosol particles in a flame environment is difficult to examine experimentally. In the case of oxidation by O₂, the semi-empirical formula of Nagle and Strickland-Constable (NSC) (1962) can be used to correlate the oxidation rate measurements for pyrolytic graphite,

$$\frac{\omega}{12} = \left(\frac{k_A P_{O_2}}{1 + k_z P_{O_2}} \right) x + k_B P_{O_2} (1 - x) \quad \text{g-carbon/cm}^2\text{-s} \quad (2.31)$$

where ω is the reaction rate per surface area and x is given by:

$$x = \left(1 + \frac{k_T}{k_B P_{O_2}} \right)^{-1} \quad (2.32)$$

where,

$$k_A = 20 \exp(-125 / RT) \quad \text{g-cm}^{-2}\text{sec}^{-1} \text{ atm}^{-1} \quad (2.33)$$

$$k_B = 4.46 \times 10^{-3} \exp(-63.6 / RT) \quad \text{g-cm}^{-2}\text{sec}^{-1} \text{ atm}^{-1} \quad (2.34)$$

$$k_T = 1.51 \times 10^{-5} \exp(-406 / RT) \quad \text{g-cm}^{-2}\text{sec}^{-1} \quad (2.35)$$

$$k_z = 21.3 \exp(17.2 / RT) \quad \text{atm}^{-1} \quad (2.36)$$

$$R = 0.00831 \quad \text{MJ/Kg mole} \quad (2.37)$$

This correlation was verified by Radcliffe and Appleton (1971) and Park and Appleton (1973) to be applicable to soot oxidation.

Puri, et al. (1994) studied the oxidation of soot in hydrocarbon diffusion flames. They found that the reactivity of soot (in terms of collision efficiency) decreased with increase in temperature, probably due to thermal annealing or radical site stabilization processes. It was also found that the OH radical was the dominant oxidizer of soot, with O_2 making only a small contribution in diffusion flames.

John et al. (1997) studied uncatalysed oxidation of a flame soot and diesel soot. They used n^{th} order model for the oxidation. The order in molecular oxygen concentration was found to be 1 for the flame soot and slightly lower than 1 for the diesel soot. The equation had the following form:

$$r = k_0' \exp(-E_a / RT) \quad (2.38)$$

$$k_0' = c(1 - \xi)^{n_\xi} \cdot P_{O_2}^{n_{O_2}} \quad (2.39)$$

$$c = \lambda S_{a_0} k_0 \quad (2.40)$$

where,

ξ = fraction of carbon that is oxidized

λ = surface concentration of active sites (cm^{-2})

k_0' = overall pre exponential factor (sec^{-1})

n_g = order of reaction

P_{O_2} = partial pressure of O_2 (atm)

S_{a_0} = initial surface area (cm^2)

k_0 = pre exponential factor (sec^{-1})

Leung and Lindstedt (1991) assumed that CO is the only product of soot oxidation and used the reaction kinetics described below:

$$R = k_3(T)S[O_2] \quad (2.41)$$

$$k_3(T) = 0.1 \times 10^5 \times T^{1/2} \times e^{-19680/T} \quad (2.42)$$

where, R is in $\text{kmol}/\text{m}^3.\text{sec}$, $k_3(T)$ is in $\text{m}^3/\text{m}^2\text{-soot}.\text{sec}$, S local surface area of soot (m^2) and $[O_2]$ is partial pressure of oxygen in Pa.

PCCL predicts soot oxidation using the semi-empirical expression (equation 2.30-2.36) reported by Nagle and Strickland-Constable (NSC) (1962). PCCL has the following reaction chemistry for soot oxidation,

The rate expression implemented in PCCL assumes soot particle size of $0.8 \mu\text{m}$ and a bulk soot density of 2.0 g/cm^3 . SNORC_iT_j.rpt gives the output report for soot oxidation kinetics and the product yields.

Chapter 3

Biomass

Biomass is biological material derived from living, or recently living organisms (www.biomassenergycentre.org.uk). It is a renewable source of energy and the use of renewable energy sources is increasing in an effort to reduce the effect of greenhouse gases production. It is recognized as the fourth largest primary energy source in the world (Li et al. 2004).

Wood and biomass can be used in a variety of ways to provide energy:

1. Direct combustion can provide heat and steam production for electricity generation
2. Gasification of biomass provides fuel gas for combustion and hence is useful as fuel for engines or turbines for electricity generation
3. Fast pyrolysis can provide a liquid fuel substitute for fuel oil (Bridgewater et al. 1999)

As with coal the proximate analysis of biomass gives the ash, moisture, volatile matter and fixed carbon content while the ultimate analysis gives the carbon, oxygen, hydrogen, nitrogen and sulfur content of the biomass. Biomass has a high percentage of volatile matter content (Biagini et al. 2002). Biomass contents can also be characterized using the chemical composition of hemicelluloses, cellulose, lignin and xylan.

Biomass pyrolysis causes thermal conversion of organics to produce liquids as the primary products. Biomass gasification means incomplete combustion of biomass resulting in production of combustible gases consisting of CO, H₂ and traces of CH₄. This mixture is called producer gas (Goswami, 1986). Biomass devolatilization is different from coal devolatilization because of 3 major reasons:

1. Biomass characterization is based on hemicelluloses, cellulose, lignin and xylan
2. The macromolecular structure of biomass consists of few condensed polyaromatic compounds
3. Product yields and release rates are highly affected by ash catalysis (Niksa et al., 2000)

The focus of this research is on biomass devolatilization.

3.1 Biomass Devolatilization

Devolatilization plays a significant role in biomass combustion processes, and it depends on the biomass form and composition. Biomass devolatilization releases light gas products such

as CO, CO₂, CH₄, H₂O, CH₃COOH, and HCOOH along with complex organic compounds (Biagini et al. 2006). PCCL predicts biomass devolatilization with the following products:

Thermal decomposition kinetics of biomass is complicated as it involves a large number of reactions. Xiu et al. (2006) and Zhao et al. (2009) described devolatilization of biomass in terms of a simple first order reaction model as follows:

$$\frac{d\alpha}{dt} = Ae^{-E/RT}(1-\alpha) \quad (3.2)$$

$$\alpha = \frac{W}{W_{\infty}} \quad (3.3)$$

where,

α = ratio of volatile mass fraction at time t to maximum volatile mass fraction

W = volatile mass fraction at time t

W_{∞} = maximum volatile mass fraction

A = Arrhenius constant

E = Activation Energy

t = residence time

Table 3.1 gives the kinetic parameters for 4 types of biomass reported by Xiu et al., 2006.

Table 3.1 Kinetic parameters for biomass devolatilization

Raw materials	$A(s^{-1})$	$E(kJ/mol)$
Wheat straw	1.05×10^3	31.65
Coconut shell	6.84×10^3	48.73
Rice Husk	1.19×10^3	39.30
Cotton stalk	2.44×10^3	40.84

Table 3.2 gives the kinetic parameters for rice husk and sawdust pyrolysis in entrained flow reactor reported by Sun et al. (2010) using equation (3.2) and (3.3).

Table 3.2 kinetic parameters for rice husk and wheat straw pyrolysis.

Raw Material	$A \text{ (s}^{-1}\text{)}$	$E \text{ (kJ/mol)}$
Rice husk	92.76	35.67
Sawdust	80.64	32.59

E. Biagini et al. (2002) defined single first order biomass devolatilization rate using a global mass balance as,

$$-\frac{dW}{dt} = k(W - W_{\infty}) \quad (3.4)$$

$$k = Ae^{\frac{-E}{RT}} \quad (3.5)$$

W = mass of the sample

W_{∞} = final solid residue of sample i.e $W_{\infty} = W_{ash} + W_{char}$

A = Arrhenius constant

E = Activation Energy

t = residence time

The kinetic parameters obtained are reported in Table 3.3

Table 3.3: Kinetic parameters for Biogran and Pine sawdust (E in kcal/mol; A in s^{-1})

Sample	Isothermal run conversion 50%	Isothermal run conversion 90%
Biogran	$E = 21.2, A = 2.2 \times 10^3$	$E = 18.1, A = 12$
Pine sawdust	$E = 29.1, A = 3.9 \times 10^3$	$E = 24.4, A = 5.7 \times 10^3$

Blasi and Branca(2001) studied primary wood degradation with three parallel reactions for the formation of the main products (char, liquid, gas). The schematic of mechanism is shown below,

$$k = k_G + k_L + k_C \quad (3.6)$$

$$k_j = Ae^{-E_j/RT}, j=G, L, C \quad (3.7)$$

Table 3.4 gives estimated values for kinetic parameters of wood pyrolysis.

Table 3.4 Kinetic constants for wood pyrolysis

	$E(\text{kJ/mol})$	$\ln A[\text{s}^{-1}]$
k_G	152.7 ± 18.2	22.2 ± 3.4
k_L	148.0 ± 17.2	23.1 ± 3.2
k_C	111.7 ± 14.3	15.0 ± 2.7

PC Coal Lab predicts biomass devolatilization kinetics and product yields using the bio-FLASHCHAIN (bio-FC) mechanism (Niksa, 2000). Bio-FC predicts primary devolatilization products along with tar and major gas species yields based on proximate and ultimate analyses of biomass. PC Coal Lab can predict the devolatilization behavior for any form of wood, grass, agricultural residue and paper. Bio-FC treats biomass as a chain copolymer of cellulose and lignin-like components. Figure 3.1 gives the schematic diagram of the bio-FC mechanism.

Currently the C₃M module does not have kinetics for biomass devolatilization. Similar to coal we can modify SFOR kinetics in C₃M for biomass devolatilization. New gas species including acetaldehyde, CH₃OH, CH₃CHO, CH₂O, C₂H₅O, NH₃ need to be added in C₃M. Reaction kinetics for the added gas species must be introduced in C₃M module.

Chapter 4

Methodology

The main aim of this research is to build a connecting bridge between PCCL and MFIX via C₃M. An interface between PCCL and C₃M that allows two-way communication between the programs is being created. The interface is designed to allow MFIX to transfer information through C₃M and PCCL, then run PCCL with input data from MFIX, and then send kinetic information back to C₃M in a form that allows C₃M to update and continue to run the MFIX simulation using the updated parameters from PCCL. Coal types whose proximate and ultimate analyses are known will be used for verification of the results. The MFIX simulation will be run initially for transport flow gasifiers. However, it is expected that all forms of gasifier will be able to be handled using the PCCL/C₃M interface in MFIX. A full description of the methodology to be used is best illustrated by examining the type and form of the results that PCCL generates. This is illustrated in the following section.

All the different protocols used in both PCCL and C₃M subroutine for describing the devolatilization and tar chemistry reactions will be studied. The differences between the reaction kinetics predicted by PCCL and MFIX via C₃M subroutines will then be determined. The parameters that are necessary to be substituted in C₃M subroutine will be noted. Powder River Basin (PRB) a sub bituminous coal has been chosen as a sample coal.

Input file Coalpc.dat and Testplan.dat will be set up in PCCL according to the operating conditions (which includes proximate and ultimate analysis of coal, temperature and pressure of gasifier, diameter of coal particle, heating rate) specified in MFIX. Wire grid/drop tube method will be chosen accordingly. Output files of interest generated by PCCL are CFDC_iT_j.rpt, FDC_iHC_j.rpt, FDC_iNG_j.rpt, FDC_iSP_j.rpt, SFORC_iT_j.rpt, SFR_iTC_j.rpt, TDC_iPR_j.rpt, TDC_iTC_j.rpt and TDC_iHC_j.rpt (i= Coal number, j=Number of operating condition).

CFDC_iT_j.rpt gives devolatilization reaction kinetic parameters. FDC_iHC_j.rpt contains the yield of hydrocarbons generated in devolatilization. FDC_iNG_j.rpt contains the yield of noncondensables gases like H₂O, CO₂ and CO produced in devolatilization. SFORC_iT_j.rpt gives the single first order reaction kinetic parameters for the formation of devolatilization product species. SFR_iTC_j.rpt contains kinetic parameter for tar cracking. TDC_iPR_j.rpt, TDC_iTC_j.rpt and TDC_iHC_j.rpt output files generate the yield of output products in the tar cracking reaction. PCCL

predicts PAH and oil as the product gas species generated from tar cracking and soot and C_2H_2 as the product gas species in secondary pyrolysis.

All the percentage yields of output products generated by PCCL are in dry ash free basis; hence they will be converted into gram basis. PAH, oil, soot and C_2H_2 will be added as new gas species in MFIX. An algorithm will be developed to transfer kinetic data generated by PCCL to MFIX in its format. Simulations similar to those described in Section 4.4 are run to verify the connecting bridge validity.

For Biomass new gas species like acetaldehyde, CH_3OH , CH_3CHO , CH_2O , C_2H_5O , NH_3 will be added in C_3M . SFOR kinetics will be used for biomass devolatilization.

4.1 Assumptions

1. The hydrocarbons (C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8) higher than CH_4 will be treated as CH_4 . This will simplify the simulations. Current C_3M module in MFIX does not have higher hydrocarbons other than CH_4 also in addition it does not have any reaction chemistry for these gas species.

Treating the gas species individually will increase simulation time.

Table 4.1 and Table 4.2 shows the comparison of % carbon in coal when the hydrocarbons are treated as CH_4 or accounted as individual gas species for PRB and Lignite coal respectively.

PRB Coal:

Ultimate analysis (%): C = 75.2, H = 4.6, O = 20.2

Basis: 100gm

Table 4.1 Comparison of % of C in devolatilization product yield for PRB coal

Products	% daf yield as individual species	%daf yield when higher hydrocarbon treated as CH_4	% C as individual gas species	% C when higher hydrocarbon treated as CH_4
CO_2	9.1	9.1	2.48	2.48
CO	5.6	5.6	2.40	2.40
H_2O	8.5	8.5	0	0
CH_4	3.8	6.68	2.85	4.95

C ₂ H ₄	1.5	0	1.29	0
C ₂ H ₆	0.24	0	0.19	0
C ₃ H ₆	1.14	0	0.98	0
H ₂	0.4	0.4	0	0
Tar (79.5% C)	13.4	13.4	10.65	10.65
Char	56.4	56.4	56.4	56.4
Total			77.24	76.88

Lignite Coal

Ultimate analysis (%): C = 73.2, H = 5.3, O = 20.7, N = 0.8, S = 0.1

Basis: 100gm

Table 4.2 Comparison of % of C in devolatilization product yield for Lignite coal

Products	% dry ash free	%daf yield when higher hydrocarbons treated as CH ₄	% of C as individual gas species	% of C when higher hydrocarbons treated as CH ₄
CO ₂	8.3	8.3	2.26	2.26
CO	7.7	7.7	3.30	3.30
H ₂ O	8.5	8.5	0	0
CH ₄	5.8	10.78	4.35	8.03
C ₂ H ₄	2.42	0	2.07	0
C ₂ H ₆	0.55	0	0.44	0
C ₃ H ₆	1.91	0	1.64	0
H ₂	0.97	0.97	0	0
Tar (77.2% C)	15.2	15.2	11.73	11.73
HCN	0.58	0.58	0.26	0.26
H ₂ S	0.09	0.09	0	0
Char	48.4	48.4	48.4	48.4
Total			74.45	73.98

It can be seen that % of carbon in coal is in good argument with % of carbon in product species when higher hydrocarbons are treated as CH₄

1. Molecular weight of soot is assumed to be 300 gm/mole.

3. PAH and soot has almost over 95% of carbon content. Specific heat of PAH and soot are assumed to be the same as fixed carbon.

$$CPPAH = -0.1315 + 1.341E-03*XXX - 1.087E-06*XXX*XXX + 3.06E-10*XXX*XXX*XXX$$

$$CPSOOT = -0.1315 + 1.341E-03*XXX - 1.087E-06*XXX*XXX + 3.06E-10*XXX*XXX*XXX$$

(Where XXX is the temperature in Kelvin)(MFI document)

4. Oil is a mixture of benzene, toluene, xylene (BTX). Average molecular weight of the mixture is 92 gm/mol. In addition it is assumed that the specific heat of oil is the same as toluene which has same molecular weight as oil.

$$CPOIL = (1.4014E+05 - 1.5230E+02*XXX + 6.9500E-01*XXX**2)/92 \quad (\text{Perry, 1997})$$

5. Version 4.1 of PCCL is not programmed to give kinetics of soot generation in secondary pyrolysis. In this research, it is assumed that when temperature is above 1000°C, soot and C₂H₂ will be products in the devolatilization step.

Chapter 5

Results and Discussion

Devolatilization and tar cracking are the main reactions that have to be modified in MFIX. PCCL takes into consideration the effect of different operating conditions for coal gasification; hence it is necessary to check the effects of operating conditions on coal devolatilization and tar cracking. Initially the differences in yields of devolatilization products given by MFIX and PCCL operating with the same input conditions were investigated. The parameters that must be replaced in the C₃M module for MFIX were identified.

5.1 Effect of Variations in Operating Conditions on pyrolysis of coal

5.1.1 Effect of Pressure

The devolatilization rate decreases as pressure increases according to a number of researchers. (Oh et al.1989, Niksa et al. 2003, Lee et al. 1991, Van Heek 1990).

The PCCL wire grid method was used to study the effect of varying operating pressure. The effect of pressure on devolatilization and tar cracking is expressed through the yield of products from those reactions. Powder River Basin (PRB) sub-bituminous coal was used as the sample coal.

PCCL results predict that:

1. Increase in pressure has significant effect on yields of tar and volatile matter at the same heating rate and temperature.
2. Yields of tar and volatile matter decrease as pressure increases at constant temperature and heating rate.
3. Yield of H₂ is affected by pressure only at higher temperatures; namely, it increases with an increase in pressure at constant temperature and heating rate.
4. Pressure has no significant effect on the yields of CO₂, CO, H₂O and CH₄. These results are illustrated in Figure 5.1

Figure 5.1 Effect of pressure on the yields of CO₂, CO, CH₄, tar, H₂ and total volatile matter with heating rate of 1500 °C/s at 1316 °C

5.1.2 Effect of Temperature

PCCL results show that:

1. As temperature increases at constant heating rate and pressure, the yields of CO, H₂ and total volatile matter increase as shown in Figure 5.2.
2. An increase in temperature has practically has no effect on the yields of CO₂, H₂O, tar and CH₄ at constant heating rate and pressure.

5.1.3 Effect of heating rate

Gibbins (1989) recorded an increase in yield of devolatilization products with an increase in heating rate.

PCCL results show:

1. As heating rate is increased at fixed temperature and pressure the yield of CO₂, H₂, CH₄, H₂O, CO decreases as shown in Figure 5.3.
2. Yield of tar and total volatile matter increases as heating rate is increased at constant temperature and pressure.

The effects of heating rate and temperature on predictions from PCCL are shown in Figure 5.2

Figure 5.2. Graph showing effect of temperature and heating rate on yield of H₂ at heating rate of 1500 °C/s, 15000 °C/s and 30000 °C/s.

Figure 5.3. Graph showing effect of heating rates on the yields of H₂, CH₄, CO, H₂O and CO₂ at operating temperature of 955 °C at 500 psi.

It can be seen that the effects of operating conditions predicted by PCCL are in agreement with experimental data available in the literature.

5.2 Comparison of devolatilization kinetic parameters

As discussed earlier MFIX has fixed devolatilization reaction kinetic parameters for 5 different types of coals. PCCL generates devolatilization reaction kinetic parameters considering all the operating conditions. Figure 5.4 shows the variation in devolatilization reaction rate

parameters obtained from MFIX and PCCL operated at the same operating conditions. Figure 5.4 shows that MFIX overpredicts the kinetic parameters for devolatilization reaction.

Figure 5.4 Figure showing comparison between devolatilization reaction parameters obtained from MFIX and PCCL at 844 °C for lignite TC 25 and PRB coal.

5.3 Comparison of stoichiometric coefficients

MFIX calculates the stoichiometric coefficients for devolatilization and tar cracking reactions via the C₃M subroutine. Stoichiometric coefficients for devolatilization and tar cracking reactions can be generated using the output data obtained from PCCL. Stoichiometric coefficients calculated using PCCL data for CO₂, H₂, H₂O, CO and CH₄ show much greater variations compared to those obtained from MFIX. The PCCL stoichiometric coefficients will

be substituted in the subroutine rates.f of MFIX. Figure 5.5 shows the comparison of stoichiometric coefficients obtained from MFIX and PCCL for Powder River Basin (PRB) and TC 25 lignite coals.

Figure 5.5 Comparison of Stoichiometric coefficients for devolatilization reaction generated from MFIX and PCCL for PRB and Lignite TC25 coal.

5.4 Comparison of PCCL coal devolatilization predictions with experimental results

Gibbons et al. (1989) studied the time temperature variation on coal pyrolysis. Experiments were carried out on Linby coal at 700°C with a heating rate of 1 °C/s and 1000 °C/s. Figure 5.6 shows the yield of total volatile matter obtained via experiments and PCCL using same operating conditions. Fletcher et al. (2005) studied effects of pressure on coal pyrolysis and char morphology. Total volatile matter yield was reported for Pittsburgh # 8 and Illinois # 6 at 2.5, 6, 10 and 15 atm pressures. Figure 5.7 represents the effects of pressure on total volatile matter yield obtained via experiment and PCCL. Neoh and Gannon (1984) observed rapid pyrolysis of Pittsburgh # 8 and Illinois # 6. They reported total volatile matter yield at 1600 K and 2400 K. Figure 5.8 shows a comparison of total volatile yield between experiments and PCCL using same operating conditions.

Figure 5.6 : Graph showing total volatile yield obtained for Linby coal via PCCL and experiments at same operating conditions.

Figure 5.7 : Graph showing total volatile yield obtained for Pittsburgh # 8 and Illinois # 6 via PCCL and experiment(EXP) at same operating conditions.

Figure 5.8 : Graph showing total volatile yield obtained for Pittsburgh # 8 and Illinois # 6 via PCCL and experiment at 1600 K and 2400 K.

Looking at Figures 5.6-5.8 it can be concluded that devolatilization predictions of PCCL are reasonably accurate and in good argument with the experimental results. Hence the results give confidence in using PCCL kinetics for modifying coal gasification kinetics in MFIX.

5.5 Comparison of yields of devolatilization products

A one-to-one comparison between PCCL and MFIX output was made to see the differences between yields of devolatilization products from the two programs. The wire grid method in PCCL was chosen as per the suggestion of Dr.Niksa. PCCL generates higher hydrocarbons other than CH_4 during devolatilization while MFIX does not report these gas species as output, in order to allow a comparison between the two methods, these higher hydrocarbons can be adjusted in one of two ways. The first way is to add them in to the tar and modify the tar molecular weight and the other way is simply to lump them with CH_4 . Heating rates obtained from MFIX were used as input to the wire grid method. PCCL output was collected and stoichiometric coefficients in MFIX were substituted along with rate parameters. The higher hydrocarbons were lumped into CH_4 and the calculation for this is shown in Appendix I.

In MFIX, a transport flow gasifier was chosen for simulation. Dimensions of the grid for the gasifier are $10\text{cm} \times 100\text{ cm}$. The set up is shown in Figure 5.9 and a brief description of the gasifier that was simulated is given below:

In this model coal feed is at cells 33-36 in the y direction, the pressure outlet is along cells 92-95 in the y direction. In this gasifier model, a hot air stream passes over a bed of coal that is coming in along with the recycled char. A hot nitrogen stream was also added above the feed inlet to maintain the temperature. Hence, throughout the channel the coal undergoes a gasification process and all the product gases leave via the pressure outlet. The output yields of all the gases were taken at the pressure outlet exit.

Figure 5.9 Transport flow gasifier for MFX simulation

The following parameters were used in the simulation runs:

1. Temperatures: 844°C and 1316°C
2. Sample Coal: PRB
3. Heating rate 1000°C/s
4. The simulation was run for 20 sec.
5. The following output cells in MFX were used to obtain yields of product gases at the pressure exit:

I cell: 11, 11; J cell: 92, 95; (which was the location of pressure outlet.)

Time span for which the output yield was obtained, T= 15, 20 sec and it was averaged.

6. Rate parameters obtained from PCCL data for the specified temperature and heating rate:

Table 5.1 Kinetic parameters obtained from PCCL

Temperature ° C	844	1316
<i>A</i> (1/s)	15,720	2315
<i>E</i> (cal/gmol)	9320	6370

7. When running the simulation in MFIX, only devolatilization rate was on while all other rates were turned off. Two simulations were run using the above mentioned conditions. One MFIX trial was simulated using the original C₃M subroutine parameters for the devolatilization reaction (these are designated by MC in following figures) and the other simulation used the C₃M subroutine rate parameters (like devolatilization rate parameters and stoichiometric coefficients for product gases) modified from data obtained via PCCL (which is designated as PC in the following figures)

A summary of the results are shown in Figures 5.10 and 5.11. From these figures the following observations can be made:

1. O₂, N₂, moisture and ash yields in both MFIX and PCCL correction trial are about same.
2. CO, CO₂, CH₄ and tar yields predicted by PCCL corrections are much higher than those from the original subroutine C₃M in MFIX.
3. H₂ yields predicted by MFIX are higher than those obtained from PCCL at low temperature but at higher temperature this trend reverses.
4. Fixed carbon (FC) yield from PCCL is higher than in the original MFIX run.
5. Volatile matter (VM) yield in the PCCL correction trial is lower than in the original MFI

Figure 5.10 Comparison of PCCL(PC) and MFIX(MC) simulations for CH₄ yield at same operating conditions(Temperatures 844°C and 1316°C) .

Figure 5.11 Comparison of PCCL(PC) and MFIX(MC) simulations for CO₂ yield at same operating conditions(Temperatures 844°C and 1316°C) .

5.6 Substitution for MFIX parameters using PCCL output

Before going further it was necessary to check that the parameters replaced in MFIX give the same output yield for devolatilization products as PCCL for the same operating conditions. For this comparison the moisture rate option was turned off. For the initial run, only the devolatilization reaction was modified. Parameters that needed to be changed in MFIX were:

1. In the subroutine rrates.f the devolatilization reaction parameter activation energy and Arrhenius constant are replaced by SFOR parameters obtained from PCCL.
2. In the subroutine rrates.f the stoichiometric coefficients for devolatilization reactions are replaced with stoichiometric coefficients obtained from PCCL output.
3. The tar molecular weight is modified in mfix.dat

Table 5.2 Comparison of devolatilization products obtained from PCCL and MFIX.

Products	Mass Fraction by MFIX	Mass fraction on N and O free basis by MFIX	PCCL yield in gm	PCCL yield in Mass fraction
O ₂	0.108	0	0	0
CO	0.0122	0.1149	3.869	0.1149
CO ₂	0.0202	0.1908	6.424	0.1908
CH ₄	0.0155	0.1468	4.9424	0.1468
H ₂	0.00053	0.005	0.1679	0.005
H ₂ O	0.0188	0.1778	5.986	0.1778
N ₂	0.786	0	0	0
Tar	0.032	0.3647	12.2778	0.3647

By comparing the second and last column of Table 5.2, it can be concluded that the parameters that are modified in MFIX are in good agreement with PCCL and hence the two models can be linked together.

5.7 Moisture Release

MFIX has single first order reaction kinetics for moisture release with a fixed Arrhenius constant and activation energy for 5 specific types of coals. PCCL generates moisture release flux based on the heating rate and temperature history. Simulation was run using the transport flow gasifier reactor set up described earlier in Section 5.5 with the operating conditions as follows:

- 1) Reactor temperature 1000°C.
- 2) Pressure 1.5 MPa
- 3) Coal Feed: Lignite and PRB
- 4) Only the moisture release rate was switched on, others were turned off.
- 5) Moisture release rate was modified in MFIX using moisture release flux given by PCCL.

Figure 5.12 and Figure 5.13 shows the moisture release along the reactor length using the original MFIX kinetics compared to modified PCCL kinetics for the Lignite and PRB coals respectively. It can be seen that, as the heating rate increases the PCCL moisture release curve shifts upward. It shows that PCCL takes into consideration the effect of heating rate while MFIX does not.

Figure 5.12 TheFigure showing moisture release along reactor length for Lignite coal at 900 °C and a heating rate of 1000°C/s in PCCL.

Figure 5.13 The moisture release along reactor length for PRB coal at 900 °C and heating rates of 1000°C/s and 17,496°C/s in PCCL.

5.8 Tar Cracking

MFIX uses single first order reaction (SFOR) kinetics for tar cracking. The kinetic parameters are fixed for the 5 types of coal. PCCL also gives tar cracking in SFOR kinetics but considers the effects of heating rate and operating temperature. In addition PCCL predicts PAH

and oil as additional product gas species for tar cracking. PAH and oil cannot survive over 1000°C. In this research, the tar cracking reaction is assumed to take place at temperatures below or equal to 1000°C otherwise the secondary pyrolysis reaction starts to take place.

The tar cracking simulation was run using the transport flow gasifier reactor set up described earlier in Section 5.5 with the operating conditions as follows:

- 1) Reactor temperature 900°C.
- 2) Pressure 1.5 MPa
- 3) Coal Feed: PRB coal
- 4) Heating rate used for PCCL 1000°C/s
- 5) Only moisture release, devolatilization and tar cracking reaction rates were turned on while all other gasification reactions were turned off.
- 6) Moisture release rate was modified in MFIX using the moisture release flux given by PCCL while devolatilization and tar cracking kinetic parameter were updated using SFOR parameters generated by PCCL.
- 7) PAH and oil were added as new gas species.
- 8) There was no fixed carbon generated via tar cracking.

Figure 5.14 shows the evolution of tar cracking products along the reactor length. It can be seen that the products show the expected evolution trend for all gas species. From this figure it can be concluded that tar cracking reaction kinetics in MFIX can be modified using PCCL predicted SFOR kinetics.

Figure 5.14 The evolution of gas species during tar cracking along reactor length for PRB coal at 900 °C.

5.9 Secondary Pyrolysis with soot oxidation

PAH and oil become unstable at temperatures above 1000 °C and react with secondary hydrocarbons to form soot and C₂H₂. Version 4.1 of PCCL does not give soot formation kinetics from PAH and oil but gives the total yield of soot and C₂H₂ formed in secondary pyrolysis. We have assumed for this work that only above 1000°C will secondary pyrolysis take place and for

this case the devolatilization reaction kinetics will be used to simulate the secondary pyrolysis reactions but with the yields adjusted to give the correct make of soot and C_2H_2 along with other gas species. Soot will also get oxidized in this process. Soot oxidation kinetics are given by Nagle and Strickland-Constable (NSC) (1962). Figures 5.15 and 5.16 show the simulation results for secondary pyrolysis and soot oxidation in transport flow gasifier. The operating conditions are as follows:

- 1) Reactor temperature 1000°C and 1200°C.
- 2) Pressure 1.5 MPa
- 3) Coal Feed: Lignite
- 4) Heating rate used for PCCL 1000°C/s
- 5) Only moisture release, devolatilization and soot oxidation reaction rates were turned on all other gasification reaction were turned off.
- 6) Soot oxidation rate was introduced in MFIX using the NSC model given by PCCL while devolatilization kinetic parameters were updated using SFOR parameters generated by PCCL.
- 7) Soot and C_2H_2 were added as new gas species.

Figure 5.15 The evolution of gas species during secondary pyrolysis along the reactor length for Lignite coal at 1000 °C.

Figure 5.16 The evolution of gas species during secondary pyrolysis along the reactor length for Lignite coal at 1200 °C.

5.10 Biomass Devolatilization

The yield for biomass devolatilization predicted by PCCL was compared with experimental results available in the literature.

Perez et al. (2008) reported the affect of temperature on the yield and quality of pyrolysis products of pine wood and oil malee. Figure 5.17 shows the comparison of char yield and water released generated by PCCL with experiments for oil malee pyrolysis at temperatures ranging from 350-500°C.

Couhert et al.(2009) observed the failure of the component additively rule to predict gas yields of biomass in flash pyrolysis at 950°C. Experiments were carried out on beechwood (BW), mix spruce (MS) and rice husk (RH). Figure 5.18 shows the secondary pyrolysis product yield obtained for BW, MS and RH at 950 °C from experiments (EXP) and PCCL. Yields of CO and CO₂ obtained from PCCL are considerably different from the experimental results while yields for the other gas products are comparable.

Figure 5.17 The evolution of char(A) and water (B) during oil malee pyrolysis

Figure 5.18 A comparison of secondary pyrolysis product yields obtained from experiments and PCCL for beechwood(BW), mix spruce(MS) and rice husk (RH) at 950°C.

Du pont et al. (2008) modeled the pyrolysis kinetics of beechwood and softwood. Figures 5.19 and 5.20 give the comparison between pyrolysis product yields generated by PCCL and experiments at 800 and 1000°C for beechwood and softwood.

Figure 5.19 A comparison of pyrolysis product yields obtained from experiments and PCCL for beechwood (A), softwood (B) at 800°C.

Figure 5.20 A comparison of pyrolysis product yields obtained from experiments and PCCL for beechwood (A), softwood (B) at 1000 °C.

Comparing Figures 5.17-5.20, it can be concluded that devolatilization predictions of PCCL are reasonably accurate and in good agreement with the experimental results for biomass pyrolysis. Hence the results give confidence in using PCCL kinetics for modifying biomass devolatilization kinetics in MFIX.

5.11 Algorithm

The basic idea behind the algorithm is to obtain the required kinetic parameters from PCCL to update C₃M. A seamless connection between PC Coal Lab and the C₃M is created. The interface is designed to allow MFIX to transfer information through C₃M to PC Coal Lab, run PC Coal Lab with the input data from MFIX and then sends kinetic information back to C₃M in a form that allows C₃M to update and continue the MFIX simulation using updated parameters from PC Coal Lab.

The output files generated from PCCL consists of product yields and reaction kinetics parameters for devolatilization, tar cracking and secondary pyrolysis. These results need to be converted into an acceptable format for C₃M. SFOR parameters for moisture release and devolatilization were obtained from CFDC_iT_j.rpt while product gas species yields were obtained from FDC_iHC_j.rpt, FDC_iNG_j.rpt and FDC_iTC_j.rpt. For tar cracking the SFOR and devolatilization parameters were obtained from SFTRC_iT_j.rpt. Secondary pyrolysis product yields were derived from FDC_iSP_j.rpt.

The detail mechanism of conversion is explained in appendix I. A Graphical User Interface (GUI) to link MFIX to PCCL via C₃M will be developed which will automatically do all the conversions.

The following steps illustrate how the process will work:

1. User will have to enter the coal proximate and ultimate analysis in the GUI.
2. GUI will run PCCL with same operating conditions used in MFIX.
3. GUI will update the C₃M using the new parameters obtained from PCCL.
4. MFIX simulations will be run using the updated C₃M parameters.

Chapter 6

Conclusions

The effects of temperature, pressure and heating rate on devolatilization yield predicted by PCCL was studied. PCCL predictions for devolatilization were compared to experimental measured yields and were found in good agreement with experimental data for the same operating conditions. Detailed kinetic expressions using PC Coal Lab (PCCL) were implemented for the devolatilization, tar cracking and secondary pyrolysis of a wide variety of coals in existing CFD code Multiphase Flow with Interphase Exchanges (MFIx) developed by NETL.

The C₃M code was studied in detail and the parameters in need of change were identified. An algorithm to link MFIx to PCCL via C₃M was developed. The parameters obtained from PCCL were converted into an acceptable format to update the fortran code in C₃M. The algorithm was tested using a simulation of a transport flow gasifier with the current C₃M kinetics and compared with results using modified kinetics obtained from PCCL. The algorithm is being used to develop a GUI at NETL site Morgantown by Phil Nicolletti.

PCCL predictions for biomass devolatilization were compared with experimental results and they show good agreement with experimental results.

Chapter 7

Future Work

Version 4.1 of PCCL is not programmed to give soot formation kinetics. The algorithm will be updated when suitable soot formation kinetics become available.

Future work will concentrate on developing algorithms for implementing homogeneous and heterogeneous reactions in C₃M/MFIX. The focus of this portion of the work will be on analyzing PCCL data for these reactions and to develop rate and appropriate yield equations to describe the reaction kinetics.

Furthermore, gasification reactions of soot that will occur in the gasifier must also be modeled. The heterogeneous oxidation and gasification reactions of the soot will therefore have to be modeled on an equivalent cell concentration basis and suitable algorithms to keep track of the conversion of the soot particles will be developed.

The current work considers steady state conditions in gasifier; future work will focus on unsteady state temperature profile across the reactor.

The C₃M module does not have biomass pyrolysis kinetics. Biomass pyrolysis will be studied in detail and PCCL data will be used to provide suitable kinetic parameters to C₃M. Finally the effect of ash and hetero-atoms (N and S) on devolatilization will be studied.

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Notation

d_p	Diameter of droplet	(m)
E_d	Activation energy	(cal/gmol)
ρ_s	Density of coal particle	(gm/cc)
k_d	Frequency factor	(1/s)
h_w	Heat transfer coefficient of water	(watt/m ² K)
λ_{vap}	Latent heat of vaporization	(J/mol)
X_{sH_2O}	Mass fraction of moisture content in coal	
T_p	Temperature of droplet	(K)
T_s	Temperature of solid phase	(K)
ε_s	Volume fraction of solid phase	
m_{vap}	Volumetric evaporation rate of black liquor droplet	(kg/m ³ s)
T_g	Local gas temperature	(K)
m_c	Mass of raw coal	(gm)
m_v	Rate of devolatilization	(gm/s)
R_g	Gas constant	(cal/K.mol)
V	Volatile yield at any time	(% daf)
V^*	Ultimate volatile yield	(Kg or daf %)
X_{VM}	Mass fraction of volatile matter	
Y	Volatile yield	(gm)
Y_I	Volatile yield for low activation devolatilization reaction	(gm)
Y_I^*	Maximum of Y_I	(gm)
Y_2	Volatile yield for high activation devolatilization reaction	(gm)
Y_2^*	Maximum of Y_2	(gm)
C_{tar}	Concentration of tar	(gmole/cm ³)
ω	Rate of soot oxidation	(g carbon/cm ³ sec)
ξ	Fraction of carbon oxidized	

λ	Surface concentration of active sites	(cm ⁻²)
S_{a_0}	Initial surface area	(cm ²)
$[O_2]$	Partial pressure of oxygen	(Pa)

Appendix I

Algorithm to couple PCCL and MFIX:

I.1. The reaction schemes considered in this algorithm are as follows,

Devolatilization only:

Devolatilization with tar cracking:

Devolatilization with soot formation or secondary pyrolysis:

Stoichiometric coefficients for PAH, oil, soot, and C₂H₂ are obtained from PCCL.

I.1.1. User has to select the reaction for which PCCL data will be extracted:

1. Devolatilization
2. Devolatilization with Tar Cracking (PAH and oil formation)
3. Devolatilization with soot formation /secondary pyrolysis (soot and C₂H₂ formation){ soot is seen above 1000°C }


```

cp_fun2.inc
CPC2H4(XXX)= (2.83 + 28.6E-3*XXX - 8.726E-6*XXX**2)/28.
CPC2H6(XXX)= (2.247 + 38.2E-3*XXX - 11.05E-6*XXX**2)/30.
CPC3H6(XXX)= (2.247 + 38.2E-3*XXX - 11.05E-6*XXX**2)/42.
CPC3H8(XXX)= (2.41 + 57.2E-3*XXX - 17.53E-6*XXX**2)/44.
CPC6H6(XXX)= (-0.409 + 77.62E-3*XXX - 26.4E-6*XXX**2)/78.

SPECIFIC HEAT OF COAL -- IGT Coal CONversion Systems Technical Data
Book (Sec. IA30.6, pp 3-4)

CPFC(XXX)= -0.1315 + 1.341E-3*XXX - 1.087E-6*XXX*XXX
            + 3.06E-10*XXX*XXX*XXX
CPVM(XXX)= 0.1743 + 8.1E-4*XXX
CPM(XXX)= 1.00763
CPA(XXX)= 0.1442 + 1.4E-4*XXX

CPPAH(XXX)= -0.1315 + 1.341E-3*XXX - 1.087E-6*XXX*XXX
            + 3.06E-10*XXX*XXX*XXX
CPOIL=(1.4014E+05 -1.5230E+02*XXX+6.9500E-1*XXX**2)/92
CPSOOT(XXX)= -0.1315 + 1.341E-3*XXX - 1.087E-6*XXX*XXX
            + 3.06E-10*XXX*XXX*XXX
CPC2H2=(2.0011E+05 -1.1988E+03 *XXX + 3.0027*XXX**2)/26

```

Equations to calculate specific heat for oil, PAH, soot and C₂H₂

I.1.2.3. Modify the constant pressure specific heat of air calculation (C_pg(IJK)) equation with addition of new gas species in physical_prop.f

```

      MW = ZERO
      N = 1
      IF (NMAX(0) > 0) THEN
        MW = MW + SUM(X_G(IJK, :NMAX(0))/MW_G(:NMAX(0)))
        N = NMAX(0) + 1
      ENDIF
      MW = ONE/MAX(MW, OMW_MAX)
-----
      MW_MIX_G(IJK) = MW
      RO_G(IJK) = EOSG(MW, P_G(IJK), T_G(IJK))
      ROP_G(IJK) = RO_G(IJK)*EP_G(IJK)

      Constant pressure specific heat of air in cal/g.K

      C_pg(IJK) = X_g(IJK, 1)*CPO2(TGX) &
        + X_g(IJK, 2)*CPCO(TGX) + X_g(IJK, 3)*CPCO2(TGX) &
        + X_g(IJK, 4)*CPCH4(TGX) + X_g(IJK, 5)*CPH2(TGX) &
        + X_g(IJK, 6)*CPH2O(TGX) + X_g(IJK, 7)*CPN2(TGX) &
        + X_g(IJK, 8)*CPTAR(TGX) + X_g(IJK, 9)*CPOIL(TGX) &
        + X_g(IJK, 10)*CPPAH(TGX) + X_g(IJK, 11)*CPC2H2(TGX) &
        + X_g(IJK, 12)*CPSOOT(TGX)
-----
      ENDIF
      END DO

      DO M = 1, NMAX

```

Adding specific heat terms for oil, PAH, soot and C₂H₂

I.1.2.4. Total number of gas species and their molecular weight need to be modify in mfix.dat

```

FXFC = .4014
PAVM = .3298
PAM = .2227
PAA = .0461
#
! Ultimate Analysis
UAC = .5502
UAH = .0340
UAO = .1470 !@ (.1374+.0096)
UAN = 0.0 !.0095 !.0 !@ (.0134*.829)
UAS = 0.0 !0.0
#
#####
#
# Gas-phase Section
#
#####
#
# MU_g0 = 6.0E-4 !1.663E-4
# NMAX(0) = 12
#
# O2 CO CO2 CH4 H2 H2O N2 Tar OIL PAH C2H2 SOOT
# MW_g = 32.0 28.0 44.0 16.0 2.0 18.0 28. 98.0 332.0 26 300
# MW_g = 28.0
# DIF_g0 = 0.0
# MW_AVG = 28.0
#
#####
#
# Solids-phase Section
#
#####
#
# RO_s = 2.85
# D_p0 = 0.01
# NMAX(1) = 6
#
#
# MW_s(1,1) = 12.0 ! Fixed Carbon
# MW_s(1,2) = 56.0 ! Volatile Matter
# MW_s(1,3) = 18.0 ! Moisture
# MW_s(1,4) = 120.0 ! Ash
# MW_s(1,5) = 120.0

```

Total numbers of gas species are modified to 12

Molecular weights of new added gas species were updated, oil (98), PAH (332), Soot (300), C₂H₂ (26).

I.1.2.5. Modify rates.f with following variables :

Pressure term for new gas species: PPAH, PSOOT, PC2H2, POIL.

Soot oxidation kinetics variables: XYZ, TAN, KPC, TANN, KPCC, XYZZ, TANC, RXNWF.

Partial pressure calculation equation for PPAH, PSOOT, PC2H2, POIL.

```

Temperatures, Pressures, Proximate An
Rate constants, activation energies,
reaction rates
DOUBLE PRECISION TGS1X, PO2, PCO, DIFF,&
PCO2, PCH4, PH2, PH2O, PATM, PATM_MW,&
PPAH, POIL, PC2H4, PC2H6, PC3H6,&
PC2H2, PSOOT,&
K_f, R_D1, RXNA, K_a, RXNA1F, FAC,&
RXNA1B, CAR1, EP_s1,&
TGX, TS1X, EQ2, EQ3, EQ5, EQ6, A3, A4
A6, A7, A8, A9,&
RXNB, RXNB1F, RXNB1B,&
RXNC, RXNC1F, RXNC1B,&
RXND, RXND1F, RXND1B,&
RXNE, RXNEF, RXNEB,&
RXNRF, RXNSF, RXNTF, RXNUF,&
RXNRB, RXNSB, RXNTB, RXNUB,&
RXNFOB, RXNFOB, RXNF1F, RXNF1B,&
RXNF2F, RXNF2B, RXNF3F, RXNF3B,&
RXNGF, RXNGB, RXNHF, RXNHB, RXNIF, RXNIB,&
RXNK1F, RXNK1B, RXNL1F, RXNWF,&
RXNL1B, EQCaD1, K_r, JOBK,&
X_coal1, TSORB1, XYZ,&
TAN, KPC, TANN, KPCC,&
XYZZ, TANC
DOUBLE PRECISION R_tmp(0:MMA, 0:MMA)

INCLUDE 'ep_s1.inc'
INCLUDE 'function.inc'
INCLUDE 'ep_s2.inc'
R_tmp = UNDEFINED

--- Remember to include all the local variables here for parallel
--- processing
mp parallel do private(ijk, R_tmp, L, LM, M, N, TGS1X, PO2, PCO, DIFF,&
mp& PCO2, PCH4, PH2, PH2O, PATM, PATM_MW,&
mp& K_f, R_D1, RXNA, K_a, RXNA1F, FAC,&
mp& RXNA1B, CAR1, EP_s1,&
mp& TGX, TS1X, EQ2, EQ3, EQ5, EQ6, A3, A4, A5,&
mp& A6, A7, A8, A9,&
mp& RXNB, RXNB1F, RXNB1B,&

```

Add pressure term for PPAH, PSOOT, PC2H2 and POIL for double precision

Add soot oxidation reaction rate terms XYZ, TAN, KPC, TANN, KPCC, XYZZ and TANC, RXNWF for double precision

```

      No   1   2   3   4   5   6   7   8
GAS Species O2, CO, CO2, CH4, H2, H2O, N2, Tar

      No   1   2   3   4   5   6   7   8
Solids species FC, VM, Moist., Ash, CaCO3, CaMg(CO3)2, CaO, MgO

move comments tagged !car to activate carbonate decomposition

TGX = MIN(MAX_TEMP, T_g(IJK))
TGX = MIN(TGX, 500.0)
TS1X = MIN(MAX_TEMP, T_s(IJK, 1))
TSORB1 = MIN(MAX_TEMP, T_s(IJK, 1))
TGS1X = HALF * (TGX + TS1X)
TGS1X = HALF * (T_g(IJK) + TS1X)

COMPUTE PARTIAL PRESSURE of various gases IN ATM. P_g in
dynes/cm^2

PATM = P_g(IJK) / 1013000.
PATM_MW = PATM * MW_MIX_g(IJK)
PO2 = PATM_MW * X_g(IJK, 1) / MW_g(1)
PCO = PATM_MW * X_g(IJK, 2) / MW_g(2)
PCO2 = PATM_MW * X_g(IJK, 3) / MW_g(3)
PCH4 = PATM_MW * X_g(IJK, 4) / MW_g(4)
PH2 = PATM_MW * X_g(IJK, 5) / MW_g(5)
PH2O = PATM_MW * X_g(IJK, 6) / MW_g(6)
PPAH = PATM_MW * X_g(IJK, 10) / MW_g(10)
POIL = PATM_MW * X_g(IJK, 9) / MW_g(9)
PC2H2 = PATM_MW * X_g(IJK, 11) / MW_g(11)
PSOOT = PATM_MW * X_g(IJK, 12) / MW_g(12)

EP_s1 = EP_s(IJK, 1)
X_coal1 = X_s(IJK, 1, 1) + X_s(IJK, 1, 2) + X_s(IJK, 1, 3) &
+ X_s(IJK, 1, 4)

```

Partial pressure calculation equation for PAH, Soot, Oil and C2H2

I.1.2.6. Modify rates.f for soot oxidation reaction:

Soot oxidation equation given by PCCL need to be introduced in MFIX.

(When there is only devolatilization or devolatilization with tar cracking this rate will be multiplied by zero.)

```

TAN=1.51E+05 *EXP(-48800/TGX)
KPC=4.46E-03 *EXP(-7640/TGX)*(PO2)
XYZ= 1/(1+(TAN/KPC))
TANN=XYZ*(240 *EXP(-15100/TGX)*(PO2))
KPCC=1+(21.3*EXP(2060/TGX))
XYZZ=TANN/KPCC
TANC=(1-XYZ)*(5.35E-02*EXP(-7640/TGX)*(PO2))
RXNWF=(XYZZ+TANC)*(6*EP_s1/0.000008)*(X_g(IJK,12)/MW_g(12))

```

```

SOOT OXIDATION:
IF(X_g(IJK,12) .GT. ZERO) THEN
  TAN=1.51E+05 *EXP(-48800/TGX)
  KPC=4.46E-03 *EXP(-7640/TGX)*(PO2)
  XYZ= 1/(1+(TAN/KPC))
  TANN=XYZ*(240 *EXP(-15100/TGX)*(PO2))
  KPCC=1+(21.3*EXP(2060/TGX))
  XYZZ=TANN/KPCC
  TANC=(1-XYZ)*(5.35E-02*EXP(-7640/TGX)*(PO2))
  RXNWF=0*(XYZZ+TANC)*(6*EP_s1/0.000008)*(X_g(IJK,12)/MW_g(12))
ELSE
  RXNWF=ZERO
ENDIF
ReactionRates(IJK,1)=RXNWF
ReactionRates(IJK,2)=RXNWF

```

Rate multiplied by zero when only devolatilization or devolatilization with tar cracking is there.

Write the formation and consumption rates of various species:
 Obtain the rates of formation and consumption of various species
 in g/(cm³.s) from the rate expressions RXNxF and RXNB obtained in the

I.2. Input Specification for PCCL:

- Proximate analysis as received basis:

Fixed Carbon: 40.2

Volatile matter: 32.9

Moisture: 22.3

Ash: 4.6

- Ultimate analysis dry ash free basis:

C: 75.2

H: 4.6

O: 20.2

N: 0

S: 0

- Heating rate for wire grid method
- Pressure in MPascal
- Temperature in $^{\circ}\text{C}$
- Particle diameter in microns

Coal properties to be specified in coalpac.dat as shown in figure1

Operating conditions to be specified in testplan.dat as shown in figure 2

FT	Coal Label							PROXIMATE, as rec'd				ULTIMATE, daf wt. %					
								PVM	FC	H ₂ O	ASH	%C	%H	%O	%N	%S	Cal ?
A3	A40							F5.1	F5.1	F5.1	F5.1	F5.1	F5.1	F5.1	F5.1	F5.1	A1
CO	LIGNITE							43.8	41.0	14.2	1.0	73.2	5.3	20.7	0.8	0.1	N
CO	SUBBITUMINOUS							43.2	37.8	6.1	12.8	78.0	5.7	15.2	1.2	0.1	N
CO	HIGH VOLATILE BITUMINOUS	NUMBER ONE						28.2	59.6	2.6	9.6	83.2	4.8	10.6	0.9	0.6	N
CO	HIGH VOLATILE BITUMINOUS	NUMBER TWO						27.6	56.1	7.5	8.8	82.3	4.6	10.9	1.8	0.4	N
CO	HIGH VOLATILE BITUMINOUS	NUMBER THREE						39.7	40.2	1.5	18.6	82.9	6.5	6.8	1.1	2.8	N

Figure1: Input file for coal types coalpac.dat

Y	Y	Y	Y	Y	Y	Y	N	N
Y	N	N						
Y	N	N	N	N	N	N	N	N

Figure2: Input file for operating conditions testplan.dat

I.3. DEVOLATILIZATION

I.3.1. Moisture Release:

Output file to look at is,

CFDC_iT_j.rpt: { for moisture flux in kg/m²-s }

WIRE GRID SIMULATION WITH PC COAL LAB

FULL DYNAMICS

COAL CHARACTERISTICS: PRBCOAL

Ultimate, daf wt. %	Proximate, as rec wt. %
%C 75.2	Moisture 22.3
%H 4.6	Vol. Mat. 32.9
%O 20.2	Ash 4.6
%N 0.0	Fixed C 40.2
%S 0.0	

OPERATING CONDITIONS:

Coal at 25. C is heated in N₂ with 0 % O₂ to
900. C at 1000. c/s, then held for .200E+01 s.
The ambient pressure is 1.50 MPa.

FUEL PROPERTIES:

Bulk density, kg/m ³	998.
Emissance	0.900
Mean Cp, J/kg-K	0.139E+04
Swelling Factor	1.092

DRYING RATE:

Moisture, AR wt. fr.	0.223
H ₂ O Flux, kg/m ² -s	0.3036E+00
Vap. Enthalpy, J/kg	0.2572E+07

DEVOLATILIZATION PRODUCTS & RATE:

	Vol Yield	MW	C/mole	H/mole	O/mole	N/mole	S/mole
	AR wt. fr.	g/mole					
whole Primary	0.310	32.1	0.128E+01	0.245E+01	0.889E+00	0.168E-04	0.220E-04

SFOR Pars: A, 1/s = 0.2575E+03 E, kcal/mole = 6.62

VOLATILES COMBUSTION:

		Stoichiometric Coefficients per Unit Fuel Mixture										
Pri	Combustion	unit	O ₂	CO ₂	H ₂ O	NO	SO ₂	CO	H ₂	<Cp>	D ₁ H ₂ F	D ₁ H ₂ C
		mole/mole	1.451	1.283	1.224	.168E-04	.220E-04			J/gmole-K	J/gmole	J/gmole
Pri	Part Oxid	mole/mole	0.449	0.154	0.349	.168E-04	.220E-04	1.130	0.875	0.794E+02	-1.71E+06	-1.592E+06

Moisture flux in kg
(0.3036)

Moisture flux in kg/m².s
(0.3036)

Changes to be made in rates.f

The moisture flux is in kg/m².s hence convert it into gm/cm³.s, so the expression becomes,

RXNGF= (Moisture flux)*0.1* (6*EP_s1 (IJK)/D_p(IJK,1)) *X_s(IJK,1,3)

{0.1 is conversion factor}

Moisture flux

```
INITIAL STAGE KINETICS
g) COAL MOISTURE --> H2O (ARBITRARY RATE EXPRESSION)
g/ (cm^3.s)

RXNGF = 0.3036|*0.1*(6*EP_s1/D_p(IJK,1)) * X_s(IJK,1,3)
RXNGB = ZERO
ELSE
RXNGF= ZERO
RXNGB = ZERO
```


WIRE GRID SIMULATION WITH PC COAL LAB									
FULL DYNAMICS									
COAL CHARACTERISTICS: PRBCOAL									
Ultimate, daf wt. %					Proximate, as rec wt. %				
%C 75.2					Moisture 22.3				
%H 4.6					Vol. Mat. 32.9				
%O 20.2					Ash 4.6				
%N 0.0					Fixed C 40.2				
%S 0.0									
OPERATING CONDITIONS:									
Coal at 25. C is heated in N2 with 0 % O2 to 900. C at 1000.0 C/s, then held for .200E+01 s. The ambient pressure is 1.50 MPa.									
Thermal History Time,s	Temp,C	Wt.Loss daf wt. %	Ygas	Noncondensibles, daf wt. %			Yco2	Yhc	Yhcn
				Yco2	Yh2o	Yco			
.000E+00	25.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00
.897E-01	115.	0.3	0.3	0.1	0.1	0.0	0.1	0.00	
.202E+00	227.	1.4	1.3	0.4	0.4	0.2	0.3	0.00	
.314E+00	339.	5.0	3.8	1.2	1.1	0.5	0.9	0.00	
.426E+00	451.	10.8	7.8	2.5	2.4	1.1	1.9	0.00	
.538E+00	563.	21.8	13.9	4.5	4.2	2.0	3.3	0.00	
.651E+00	676.	33.2	22.3	7.1	6.6	3.3	5.2	0.00	
.763E+00	788.	38.9	26.4	8.3	7.7	4.2	6.0	0.00	
.875E+00	900.	42.2	28.9	8.9	8.3	5.0	6.5	0.00	
.947E+00	900.	42.8	29.5	9.0	8.4	5.3	6.6	0.00	
.103E+01	900.	43.1	29.8	9.0	8.4	5.4	6.6	0.00	
.111E+01	900.	43.3	29.9	9.1	8.4	5.5	6.6	0.00	
.121E+01	900.	43.5	30.1	9.1	8.5	5.6	6.6	0.00	
.132E+01	900.	43.6	30.2	9.1	8.5	5.6	6.6	0.00	
.143E+01	900.	43.7	30.3	9.1	8.5	5.7	6.6	0.00	
.156E+01	900.	43.8	30.4	9.1	8.5	5.7	6.6	0.00	
.170E+01	900.	43.9	30.5	9.1	8.5	5.8	6.6	0.00	
.186E+01	900.	44.0	30.5	9.1	8.5	5.8	6.7	0.00	
.203E+01	900.	44.0	30.6	9.1	8.5	5.8	6.7	0.00	
.222E+01	900.	44.1	30.7	9.1	8.5	5.9	6.7	0.00	
.243E+01	900.	44.2	30.7	9.1	8.5	5.9	6.7	0.00	
.288E+01	900.	44.3	30.8	9.2	8.5	5.9	6.7	0.00	

**% daf yield of CO₂, H₂O, CO and CH₄
(total hydrocarbon yield is assumed to be CH₄ yield)**

- FDCiHCj.rpt:[for % dry ash free basis yield of H2(0.55)]

WIRE GRID SIMULATION WITH PC COAL LAB												
FULL DYNAMICS												
COAL CHARACTERISTICS: PRBCOAL												
Ultimate, daf wt. %						Proximate, as rec wt. %						
%C 75.2						Moisture 22.3						
%H 4.6						Vol. Mat. 32.9						
%O 20.2						Ash 4.6						
%N 0.0						Fixed C 40.2						
%S 0.0												
OPERATING CONDITIONS:												
Coal at 25. C is heated in N2 with 0 % O2 to 900. C at 1000.0 C/s, then held for .200E+01 s. The ambient pressure is 1.50 MPa.												
Thermal History Time, s	Tmp, C	Wt. Loss daf wt. %	HCS	CH4	C2H4	C2H6	C3H6	C3H8	H2	H2S		
.000E+00	25.	0.0	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00		
.897E-01	115.	0.3	0.1	0.0	0.01	0.00	0.01	0.00	0.00	0.00		
.202E+00	227.	1.4	0.3	0.2	0.07	0.01	0.06	0.00	0.00	0.00		
.314E+00	339.	5.0	0.9	0.5	0.20	0.03	0.15	0.00	0.00	0.00		
.426E+00	451.	10.8	1.9	1.1	0.42	0.07	0.32	0.00	0.00	0.00		
.538E+00	563.	21.8	3.3	1.9	0.74	0.12	0.56	0.00	0.01	0.00		
.651E+00	676.	33.2	5.2	2.9	1.17	0.19	0.89	0.00	0.04	0.00		
.763E+00	788.	38.9	6.0	3.4	1.36	0.22	1.04	0.00	0.09	0.00		
.875E+00	900.	42.2	6.5	3.7	1.46	0.23	1.12	0.00	0.20	0.00		
.947E+00	900.	42.8	6.6	3.7	1.48	0.23	1.13	0.00	0.26	0.00		
.103E+01	900.	43.1	6.6	3.7	1.49	0.24	1.13	0.00	0.30	0.00		
.111E+01	900.	43.3	6.6	3.7	1.49	0.24	1.14	0.00	0.33	0.00		
.121E+01	900.	43.5	6.6	3.7	1.49	0.24	1.14	0.00	0.35	0.00		
.132E+01	900.	43.6	6.6	3.8	1.50	0.24	1.14	0.00	0.38	0.00		
.143E+01	900.	43.7	6.6	3.8	1.50	0.24	1.14	0.00	0.40	0.00		
.156E+01	900.	43.8	6.6	3.8	1.50	0.24	1.14	0.00	0.42	0.00		
.170E+01	900.	43.9	6.6	3.8	1.50	0.24	1.15	0.00	0.44	0.00		
.186E+01	900.	44.0	6.7	3.8	1.50	0.24	1.15	0.00	0.46	0.00		
.203E+01	900.	44.0	6.7	3.8	1.50	0.24	1.15	0.00	0.48	0.00		
.222E+01	900.	44.1	6.7	3.8	1.50	0.24	1.15	0.00	0.50	0.00		
.243E+01	900.	44.2	6.7	3.8	1.50	0.24	1.15	0.00	0.51	0.00		
.288E+01	900.	44.3	6.7	3.8	1.50	0.24	1.15	0.00	0.55	0.00		

% daf basis yield of H₂(0.55)

- FDC_iTC_j.rpt : [for % dry ash free basis yield of Tar(13.4) ,molecular weight(291.9)]

WIRE GRID SIMULATION WITH PC COAL LAB												
FULL DYNAMICS												
COAL CHARACTERISTICS: PRBCOAL												
Ultimate, daf wt.%						Proximate, as rec wt. %						
%C 75.2						Moisture 22.3						
%H 4.6						Vol. Mat. 32.9						
%O 20.2						Ash 4.6						
%N 0.0						Fixed C 40.2						
%S 0.0												
OPERATING CONDITIONS:												
Coal at 25. C is heated in N2 with 0 % O2 to 900. C at 1000.0 C/s, then held for .200E+01 s. The ambient pressure is 1.50 MPa.												
Thermal History			wt. Loss		Tar Characteristics							
Time, s	Tmp, C	daf wt. %	Ytar	Mn, g/m	% C	% H	% O	% N	% S			
.000E+00	25.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.897E-01	115.	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.202E+00	227.	1.4	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.314E+00	339.	5.0	1.2	210.3	74.2	5.3	20.5	0.0	0.0	0.0	0.0	0.0
.426E+00	451.	10.8	2.9	236.5	74.4	5.5	20.1	0.0	0.0	0.0	0.0	0.0
.538E+00	563.	21.8	7.8	291.1	75.7	5.6	18.7	0.0	0.0	0.0	0.0	0.0
.651E+00	676.	33.2	10.9	299.1	77.3	5.6	17.1	0.0	0.0	0.0	0.0	0.0
.763E+00	788.	38.9	12.6	295.8	78.7	5.6	15.6	0.0	0.0	0.0	0.0	0.0
.875E+00	900.	42.2	13.3	293.3	79.4	5.7	15.0	0.0	0.0	0.0	0.0	0.0
.947E+00	900.	42.8	13.4	292.7	79.4	5.7	14.9	0.0	0.0	0.0	0.0	0.0
.103E+01	900.	43.1	13.4	292.5	79.5	5.7	14.9	0.0	0.0	0.0	0.0	0.0
.111E+01	900.	43.3	13.4	292.3	79.5	5.7	14.8	0.0	0.0	0.0	0.0	0.0
.121E+01	900.	43.5	13.4	292.2	79.5	5.7	14.8	0.0	0.0	0.0	0.0	0.0
.132E+01	900.	43.6	13.4	292.2	79.5	5.7	14.8	0.0	0.0	0.0	0.0	0.0
.143E+01	900.	43.7	13.4	292.1	79.5	5.7	14.8	0.0	0.0	0.0	0.0	0.0
.156E+01	900.	43.8	13.4	292.1	79.5	5.7	14.8	0.0	0.0	0.0	0.0	0.0
.170E+01	900.	43.9	13.4	292.0	79.5	5.7	14.8	0.0	0.0	0.0	0.0	0.0
.186E+01	900.	44.0	13.4	292.0	79.5	5.7	14.8	0.0	0.0	0.0	0.0	0.0
.203E+01	900.	44.0	13.4	292.0	79.5	5.7	14.8	0.0	0.0	0.0	0.0	0.0
.222E+01	900.	44.1	13.4	292.0	79.5	5.7	14.8	0.0	0.0	0.0	0.0	0.0
.243E+01	900.	44.2	13.4	292.0	79.5	5.7	14.8	0.0	0.0	0.0	0.0	0.0
.288E+01	900.	44.3	13.4	291.9	79.5	5.7	14.8	0.0	0.0	0.0	0.0	0.0

% daf yield of tar (13.4)

Molecular weight of tar (291.9)

I.3.2.2. Convert % daf basis yields into gm yield

If X is the % daf basis yield then gm yield will be $[X \times (FC + VM) / 100]$

(here $FC + VM = 40.2 + 32.9 = 73.1$)

Products	% yield daf	yield in gm
CO	5.9	$5.9 \times 0.731 = 4.3129$
CO₂	9.2	$9.2 \times 0.731 = 6.7252$
CH₄	6.7	$6.7 \times 0.731 = 4.8977$
H₂	0.55	$0.55 \times 0.731 = 0.4021$
H₂O	8.5	$8.5 \times 0.731 = 6.2135$
tar	13.4	$13.4 \times 0.731 = 9.7954$

I.3.2.3. Find total VM by summation of all gm yields:

Total VM = $\sum$ (Yield in gm of all devolatilization products)

Products	yield in gm
CO	4.3129
CO₂	6.7252
CH₄	4.8977
H₂	0.4021
H₂O	6.2135
tar	9.7954
VM	32.3468

I.3.2.4 Convert gm yield into mass fractions (per 1 gm of VM):

Stoichiometric coefficient = (Yield in gm of product) / (VM yield in gm)

For tar just to match stoichiometric coefficients summation as one,

Stoichiometric coefficient of Tar = $1 - \text{Sum (Stoichiometric coefficients of CO, CO}_2, \text{CH}_4, \text{H}_2, \text{H}_2\text{O})$

Products	Yield in gm	Stoichiometric Coefficient	Stoichiometric Coefficient
CO	4.3129	0.1333	BETAD(2)
CO ₂	6.7252	0.2079	BETAD(3)
CH ₄	4.8977	0.1514	BETAD(4)
H ₂	0.4021	0.0124	BETAD(5)
H ₂ O	6.2135	0.1921	BETAD(6)
tar	9.7954	{1-0.1333-0.2079-0.1514-0.0124-0.1921}=0.3029	ALPHAD
VM	32.3468	1.0000	

I.3.2.5. Changes to be made in rrates.f of MFIX:

- (modifying rrates.f) :Change devolatilization rate parameters AKD(A)(257.5) and AED(E)(6620)

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rrates.f - WordPad
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RXNC1F = RXNC * PCO2
RXNC1B = RXNC * PCO*PCO/EQ5

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! (2) CO
R_gp(IJK, 2) = (2. * (RXNB1F) + RXNB1F &
+ 2. * (RXNC1F) + RXNEB) * MW_g(2) &
+ (RXNHF - RXNHB) * BETAD(2) &
+ RXNIF * BETAC(2)
IF(X_g(IJK, 2) .GT. ZERO) THEN
RoX_gc(IJK, 2) = (RXNB1B + 2. * (RXNC1B) &
+ RXNEF + RXNF2F) * MW_g(2) / X_g(IJK, 2)
ELSE
RoX_gc(IJK, 2) = 1.0e-9
ENDIF

! (3) CO2
R_gp(IJK, 3) = (RXNC1B + RXNEF + RXNF1F + RXNF2F &
+ F3_3 * RXNF3F &
+ RXNK1F &
+ RXNL1F &
) * MW_g(3) &
+ (RXNHF - RXNHB) * BETAD(3) &
+ RXNIF * BETAC(3)
IF(X_g(IJK, 3) .GT. ZERO) THEN
RoX_gc(IJK, 3) = (RXNC1F + RXNEB + RXNL1B) &
* MW_g(3) / X_g(IJK, 3)
ELSE
RoX_gc(IJK, 3) = 1.0e-9
ENDIF

! (4) CH4
R_gp(IJK, 4) = HALF * (RXND1F) * MW_g(4) &
+ (RXNHF - RXNHB) * BETAD(4) + RXNIF * BETAC(4)
IF(X_g(IJK, 4) .GT. ZERO) THEN
RoX_gc(IJK, 4) = ((RXND1B) * HALF + RXNF1F) * MW_g(4) &
/ X_g(IJK, 4)
ELSE
RoX_gc(IJK, 4) = 1.0e-9
ENDIF

! (5) H2
R_gp(IJK, 5) = (RXNB1F + RXND1B + RXNEF) &
* MW_g(5) + (RXNHF - RXNHB) * BETAD(5) &
+ RXNIF * BETAC(5)
IF(X_g(IJK, 5) .GT. ZERO) THEN
RoX_gc(IJK, 5) = (RXNB1B + RXND1F + RXNEB &

```

Stoichiometric Coefficient of CO (0.1333)

Stoichiometric Coefficient of CO₂ (0.2079)

Stoichiometric Coefficient of CH₄ (0.1514)

Stoichiometric Coefficient of H₂ (0.0124)

```

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! (6) H2O
R_gp(IJK, 6) = (RXNB1B + RXNEB + 2. * RXNF0F &
+ 2. * RXNF1F + F3_6 * RXNF3F) * MW_g(6) &
+ RXNGF + (RXNHF - RXNHB) * BETAD(6) &
+ RXNIF * BETAC(6)
IF(X_g(IJK, 6) .GT. ZERO) THEN
RoX_gc(IJK, 6) = (RXNB1F + RXNEF) * MW_g(6) &
/ X_g(IJK, 6)
ELSE
RoX_gc(IJK, 6) = 1.0e-9
ENDIF

! (7) N2
! inert here
R_gp(IJK, 7) = ZERO
RoX_gc(IJK, 7) = ZERO

! (8) TAR
R_gp(IJK, 8) = (RXNHF - RXNHB) * ALPHAD
IF(X_g(IJK, 8) .GT. SMALL_NUMBER) THEN
RoX_gc(IJK, 8) = (RXNF3F * MW_g(8) + RXNIF) / X_g(IJK, 8)
ELSE
RoX_gc(IJK, 8) = 1.0e-9
ENDIF

```

Stoichiometric Coefficient of H₂O (0.1921)

Stoichiometric Coefficient of Tar (0.3029)

I.3.2.6. Changes to be made in usr0.f:

Stoichiometric coefficient used to calculate heat of devolatilization (HEATD) need to be replaced with new calculated coefficients.

```

ENDIF
IF(HHVT .EQ. UNDEFINED)THEN
  HHVT = 8080. * FTC + 34444.4 * (FTH - FTQ/8.) + 2277.8 * FTS
ENDIF
HHVC = ZERO
HHVT = ZERO

HEAT OF DEVOLATILIZATION REACTION (cal/g-VM)

IF( HHVC .GT. ZERO)THEN
  HEATD = (-HHVC -&
    PAVM * ( (-HHVT) * ALPHAD +&
      ( -2415.6 ) * BETAD(2) +&
      ( -13300.0 ) * BETAD(4) +&
      ( -12043.9 ) * BETAD(11) +&
      ( -12427.3 ) * BETAD(12) +&
      ( -12059.1 ) * BETAD(13) +&
      ( -10012.6 ) * BETAD(14) +&
      ( -34158.5 ) * BETAD(5) +&
      ( -584.4 ) * BETAD(6) +&
      ( -3956.5 ) * BETAD(7) +&
      ( -5394.2 ) * BETAD(9) ) )
    PAFC * (-7837.7) )/I
HEAT OF CRACKING REACTION (cal/g-Tar)

```

ALPHAD=0.3029
BETAD(2)=0.1333
BETAD(4)=0.1514
BETAD(5)=0.0124
BETAD(6)=0.1921
Rest of them are zero

I.4. Tar Cracking Algorithm:

I.4.1. Modifying Input files in PC Coal Lab (PCCL)

There is no change in “Coalpc.dat”.

While specifying operating conditions in “Testplan.dat”, ninth entry in sixth row must be specified as “T” for tar cracking.

CF	TR	TS	OR	Gas	T _{initial}	T _{gas}	Q, °C/s	%O ₂	P, MPa	Time, s	D _p , μm
A2	A3	A5	A3	A3	F6.0	F6.0	F7.0	F6.1	F6.2	F8.3	F6.1
01	WG	FFTG	UD	N2	25.	1000.	200.	0.0	1.50	2.125	90.0
UC	WG	FFTG	UD	N2	25.	600.	60.	0.0	0.10	25.000	90.0
03	WG	FFTG	UD	N2	25.	558.	2000.	0.0	0.10	2.233	90.0
04	WG	FFTG	UD	N2	25.	558.	2000.	0.0	0.10	2.233	0.0
05	WG	FFTG	UD	N2	25.	725.	2000.	0.0	0.10	2.150	0.0
Y	Y	Y	Y	Y	N	T	Y	Y	Y	Y	Y
Y	N	N	Y	Y	Y	Y	Y	Y	Y	Y	Y
Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y

For Tar Cracking 9th Entry in sixth row must be T.

I.4.2. Moisture release and devolatilization are the initial steps in the tar cracking mechanism.

For moisture release and devolatilization kinetics user should refer back to algorithm described before for devolatilization step (I.3) only.

I.4.3. Output files to look for:

- SRTRC_iT_j.rpt: [for Arrhenius constant/frequency factor (A) in 1/sec; Activation Energy (E) in kcal/mol](A=17.2/s; E=5800cal/mol)

- **SRTRC_iT_j.rpt:** To get stoichiometric coefficients for the tar cracking reaction where PAH, oil, CO, CO₂, CH₄, H₂ and H₂O are the products formed during tar cracking. We need to get mass fractions of these products from the output file.

I.4.4. Assigning mass fraction to respective gas species:

Product	Mass fraction	Mass fraction in MFIx rrates.f
PAH	0.6290	
oil	0.1220	
CO	0.0587	BETAC(2)
CO ₂	0.0695	BETAC(3)
H ₂	0	BETAC(5)
H ₂ O	0.0605	BETAC(6)
CH ₄ (As other hydrocarbons can not be lumped in CH ₄)	1-(0.6290+0.1220 +0.0587+0.0695+0 +0.0605)=0.0603	BETAC(4)

I.4.5. Changes to be made in rrates.f of MFIx:

- Change the kinetic parameters for tar cracking reaction. AKC and AEC to be replaced by new Arrhenius constant and Activation energy obtained from PCCL.

[AKC=17.2 sec⁻¹, AEC= 5800 cal/mol]

```

A5 = EP_s1*PAA*RO_s(1)*EXP(-8.91+5553.0/TGS1X)
RXNE = A3*A4*A5*EP_g(IJK)
RXNEF = RXNE * PCO*PH2O
RXNEB = RXNE * PCO2*PH2/EQ3

i) TAR --> CHAR + GASES      g/(cm^3.s)
      (1.0)      (alphac)      (1-alphac = Sum of betac's)
It is assumed that tar cracking is catalyzed by char and that
the resulting carbon is deposited on char.

IF(EP_s1 .GT. ZERO) THEN
  RXNIF = AKC*EXP(-AEC/(1.987*TGX))*ROP_g(IJK)*X_g(IJK, 8)
ELSE
  RXNIF = ZERO
ENDIF
RXNIB = ZERO

```

AKC to be replaced with
Arrhenius constant obtained
from SFTRC_iT_j.rpt
(here AKC= 17.2 sec⁻¹)

AEC to be replaced with
Activation Energy Obtained
from SFTRC_iT_j.rpt
(here AEC =5800 cal/mol)

- Substitute the stoichiometric coefficient for the product species of tar cracking reaction in rates.f

Change stoichiometric coefficients BETAC (2-6) and add stoichiometric coefficients for Oil and PAH.

<pre> (2) CO R_gp(IJK, 2) = (2. * (RXNA1F) + RXNB1F & + 2. * (RXNC1F) + RXNEB) * MW_g(2) & + (RXNHF - RXNHB) * BETAD(2) & + RXNIF * BETAC(2) IF (X_g(IJK, 2) .GT. ZERO) THEN RoX_gc(IJK, 2) = (RXNB1B + 2. * (RXNC1B) & + RXNEF + RXNF2F) * MW_g(2) / X_g(IJK, 2) ELSE RoX_gc(IJK, 2) = 1.0e-9 ENDIF ! ! (3) CO2 R_gp(IJK, 3) = (RXNC1B + RXNEF + RXNF1F + RXNF2F & + F3_3 * RXNF3F & + RXNK1F & + RXNL1F &) * MW_g(3) & + (RXNHF - RXNHB) * BETAD(3) & + RXNIF * BETAC(3) IF (X_g(IJK, 3) .GT. ZERO) THEN RoX_gc(IJK, 3) = (RXNC1F + RXNEB + RXNL1B) & * MW_g(3) / X_g(IJK, 3) ELSE RoX_gc(IJK, 3) = 1.0e-9 ENDIF ! ! (4) CH4 R_gp(IJK, 4) = HALF * (RXND1F) * MW_g(4) & + (RXNHF - RXNHB) * BETAD(4) + RXNIF * BETAC(4) IF (X_g(IJK, 4) .GT. ZERO) THEN RoX_gc(IJK, 4) = ((RXND1B) * HALF + RXNF1F) * MW_g(4) & / X_g(IJK, 4) ELSE RoX_gc(IJK, 4) = 1.0e-9 ENDIF ! ! (5) H2 R_gp(IJK, 5) = (RXNB1F + RXND1B + RXNEF) & * MW_g(5) + (RXNHF - RXNHB) * BETAD(5) & + RXNIF * BETAC(5) </pre>	<p>Stiochiometric coefficient of CO (0.0587)</p> <p>Stiochiometric coefficient of CO₂ (0.0695)</p> <p>Stiochiometric coefficient of CH₄ (0.0603)</p> <p>Stiochiometric coefficient of H₂ (0)</p>
---	---

```

(6) H2O
R_gp(IJK, 6) = (RXNB1B + RXNEB + 2. * RXNFOF &
               + 2. * RXNF1F + F3_6 * RXNF3F) * MW_g(6) &
               + RXNGF + (RXNHF - RXNHB) * BETAD(6) &
               + RXNIF * BETAC(6)
IF (X_g(IJK, 6) .GT. ZERO) THEN
  RoX_gc(IJK, 6) = (RXNB1F + RXNEF) * MW_g(6) &
                  / X_g(IJK, 6)
ELSE
  RoX_gc(IJK, 6) = 1.0e-9
ENDIF

```

Stiochiometric coefficient of H₂O (0.0605)

```

END IF
(9) OIL
R_gp(IJK, 9) = RXNIF* 0.122
(10) PAH
R_gp(IJK, 10) = RXNIF* 0.6290

```

**Stoichiometric coefficient
for Oil (0.122) and PAH
(0.629)**

I.4.6. Changes to be made in usr0.f:

Stoichiometric coefficients used to calculate heat of cracking reaction need to be replaced with new coefficients.

```

HEAT OF CRACKING REACTION (cal/g-Tar)

HEATC = -HHVT - (&
  (-7837.7) * ALPHAC +&
  (-2415.6) * BETAC(2) +&
  (-13300.0) * BETAC(4) +&
  (-12043.9) * BETAC(11) +&
  (-12427.3) * BETAC(12) +&
  (-12059.1) * BETAC(13) +&
  (-10012.6) * BETAC(14) +&
  (-34158.5) * BETAC(5) +&
  (-584.4) * BETAC(6) +&
  (-3956.5) * BETAC(7) +&
  (-5394.2) * BETAC(9) )
ELSE
  HEATD = 0.0
  HEATC = 0.0

```

**BETAC(2)=0.0587
BETAC(4)=0.0603
BETAC(5)=0.0
BETAC(6)=0.0605
rest are zero.**

I.5. Secondary Pyrolysis with soot oxidation:

I.5.1. Algorithm for moisture release to be referred back to devolatilization step (I.3) described before.

I.5.2. Output file to look at is:

- CFDC_iT_j.rpt : [for Arrhenius constant/frequency factor (A) in 1/sec; Activation Energy (E) in kcal/mol]($A=257.5$ 1/s; $E=6620$ kcal/mol)

WIRE GRID SIMULATION WITH PC COAL LAB

FULL DYNAMICS

COAL CHARACTERISTICS: PRBCOAL

Ultimate, daf wt. %	Proximate, as rec wt
%C 75.2	Moisture 22.3
%H 4.6	Vol. Mat. 32.9
%O 20.2	Ash 4.6
%N 0.0	Fixed C 40.2
%S 0.0	

OPERATING CONDITIONS:

Coal at 25. C is heated in N2 with 0 % O2 to
900. C at 1000. C/s, then held for 200E+01 s.
The ambient pressure is 1.50 MPa.

FUEL PROPERTIES:

Bulk density, kg/m3	998.
Emittance	0.900
Mean Cp, J/kg-K	0.139E+04
Swelling Factor	1.092

DRYING RATE:

Moisture, AR wt. fr.	0.223
H2O Flux, kg/m2-s	0.3036E+00
Vap. Enthalpy, J/kg	0.257E+07

DEVOLATILIZATION PRODUCTS & RATE:

	Vol yield	Mw	C/mole	H/mole	O/mole	N/mole	S/mole
	AR wt. fr.	g/mole					
whole Primary	0.310	32.1	0.128E+01	0.245E+01	0.889E+00	0.168E-04	0.220E-04

SFOR Pars: A, 1/s = 0.2575E+03 E, kcal/mole = 6.62

VOLATILES COMBUSTION:

Stoichiometric Coefficients per Unit Fuel Mixture									
	Units	O2	CO2	H2O	NO	SO2	CO	H2	
Pri Combustion	mole/mole	1.451	1.283	1.224	.168E-04	.220E-04			
Pri Part Oxid	mole/mole	0.449	0.154	0.349	.168E-04	.220E-04	1.130	0.875	

<Cp>	D1HF	D1HC
J/gmole-K	J/gmole	J/gmole
0.794E+02	-.171E+06	-.592E+06
0.794E+02	-.171E+06	0.281E+05

Arrhenius constant (A) to be replaced as AKD in rrates.f

Activation Energy (E) to be replaced as AED in rrates.f

- FDC_iSP_j. rpt: This files gives the yields of product formed after devolatilization and secondary pyrolysis.

WIRE GRID SIMULATION WITH PC COAL LAB

FULL DYNAMICS

COAL CHARACTERISTICS: PRBCOAL

Ultimate, daf wt. %

Proximate, as rec wt. %

Moisture 22.2

Vol. Mat. 1.0

Ash 1.0

Fixed C 53.0

Yield of Soot in %daf

Yield of CH₄ in %daf

Yield of C₂H₂ in %daf

OPERATING CONDITIONS:

Coal at 25. C is heated in N₂ with 0 % O₂ to 900. C at 1000.0 C/s, then held for 202E+01 s. The ambient pressure is 1.50 MPa.

Yield of CO₂ in %daf

Thermal History Time, s	Temp, C	Wt. Loss daf wt. %	Soot	CH ₄	C ₂ H ₂	H ₂	CO	CO ₂	H ₂ O	HCN	H ₂ S
.000E+00	25.	0.0	0.0	0.0	0.0	0.00	0.0	0.0	0.0	0.0	0.0
.897E-01	115.	0.3	0.0	0.0	0.1	0.01	0.0	0.0	0.0	0.0	0.0
.202E+00	227.	1.4	0.1	0.0	0.2	0.04	0.0	0.0	0.0	0.0	0.0
.314E+00	339.	5.0	1.1	0.1	0.3	0.20	0.9	1.2	1.1	0.00	0.0
.426E+00	451.	10.8	2.6	0.2	0.5	0.44	2.1	2.5	2.4	0.00	0.0
.538E+00	563.	21.8	7.1	0.2	0.8	0.98	4.5	4.5	4.2	0.00	0.0
.651E+00	676.	33.2	10.0	0.3	1.2	1.44	6.6	7.1	6.6	0.00	0.0
.763E+00	788.	38.9	11.5	0.4	1.7	1.70	7.7	8.3	7.7	0.00	0.0
.875E+00	900.	42.2	12.1	0.4	2.0	1.90	8.5	8.9	8.3	0.00	0.0
.947E+00	900.	42.8	12.2	0.4	2.1	1.98	8.8	9.0	8.4	0.00	0.0
.103E+01	900.	43.1	12.2	0.4	2.1	2.02	8.9	9.0	8.4	0.00	0.0
.111E+01	900.	43.3	12.3	0.4	2.1	2.05	9.0	9.1	8.4	0.00	0.0
.121E+01	900.	43.5	12.3	0.4	2.1	2.08	9.1	9.1	8.5	0.00	0.0
.132E+01	900.	43.6	12.3	0.4	2.1	2.11	9.1	9.1	8.5	0.00	0.0
.143E+01	900.	43.7	12.3	0.4	2.1	2.13	9.2	9.1	8.5	0.00	0.0
.156E+01	900.	43.8	12.3	0.4	2.1	2.15	9.2	9.1	8.5	0.00	0.0
.170E+01	900.	43.9	12.3	0.4	2.1	2.18	9.2	9.1	8.5	0.00	0.0
.186E+01	900.	44.0	12.3	0.4	2.1	2.19	9.3	9.1	8.5	0.00	0.0
.203E+01	900.	44.0	12.3	0.4	2.1	2.21	9.3	9.1	8.5	0.00	0.0
.222E+01	900.	44.1	12.3	0.4	2.1	2.23	9.3	9.1	8.5	0.00	0.0
.243E+01	900.	44.2	12.3	0.4	2.1	2.25	9.4	9.1	8.5	0.00	0.0
.290E+01	900.	44.3	12.3	0.4	2.2	2.28	9.4	9.2	8.5	0.00	0.0

Yield of H₂ in %daf Yield of CO in %daf Yield of H₂O in %daf

I.5.3 Convert % daf basis yields into gm yield

If X is the % daf basis yield then gm yield will be $[X \times (FC + VM) / 100]$

(here $FC + VM = 40.2 + 32.9 = 73.1$)

Products	% yield daf	yield in gm
CO	9.4	$9.4 \times 0.731 = 6.8714$
CO ₂	9.2	$9.2 \times 0.731 = 6.7252$
CH ₄	0.4	$0.4 \times 0.731 = 0.2924$
H ₂	2.28	$2.28 \times 0.731 = 1.6667$
H ₂ O	8.5	$8.5 \times 0.731 = 6.2135$
C ₂ H ₂	2.2	$2.2 \times 0.731 = 1.6082$
soot	12.3	$12.3 \times 0.731 = 8.9913$

I.5.4. Find total VM by summation of all gm yields:

Total VM= $\sum$ (Yield in gm of all devolatilization and secondary pyrolysis products)

Products	yield in gm
CO	6.8714
CO ₂	6.7252
CH ₄	0.2924
H ₂	1.6667
H ₂ O	6.2135
C ₂ H ₂	1.6082
soot	8.9913
VM	32.3687

I.5.5. Convert gm yield into mass fractions (per 1 gm of VM):

Stoichiometric coefficient= (Yield in gm of product) / (VM yield in gm)

For Soot just to match stoichiometric coefficients summation as one,

Stoichiometric coefficient of Soot= 1- Sum (Stoichiometric coefficients of CO, CO₂, CH₄, H₂, H₂O, C₂H₂)

Products	Yield in gm	Stoichiometric Coefficient	Stoichiometric Coefficient
CO	6.8714	0.2123	BETAD(2)
CO ₂	6.7252	0.2078	BETAD(3)
CH ₄	0.2924	0.0090	BETAD(4)
H ₂	1.6667	0.0515	BETAD(5)
H ₂ O	6.2135	0.1920	BETAD(6)
C ₂ H ₂	1.6082	0.0497	
soot	8.9913	{ 1-0.2123-0.2078-0.0090-0.515-0.1920-0.0497)=0.2777	
VM	32.3687	1.0000	

I.5.6. Changes to be made in MFIX.:

- (modifying rates.f) :Change devolatilization rate parameters AKD(A) (257.5 sec^{-1}) and AED(E) (6620 cal/mol)

```

rates.f - WordPad
File Edit View Insert Format Help

RXNC1F = RXNC * PCO2
RXNC1B = RXNC * PCO*PCO/EQ5

!
!
! d) (1/2)C + H2 --> (1/2)CH4 g-mole/(cm^3.s)
! Wen et al. (1982)
!
AKD needs to be replace by A obtained from PCCL

EQ6 = EXP ( - 13.4289 + 10998.5 / TGS1X )
RXND = EXP( - 7.0869 - 8077.5 / TGS1X ) * CAR1
RXND1F = RXND * PH2
RXND1B = RXND * SQRT ( MAX(PCH4,ZERO) / EQ6 )

!
! INITIAL STAGE KINETICS
! g) COAL MOISTURE --> H2O (ARBITRARY RATE EXPRESSION)
! g/(cm^3.s)
!
AED needs to be replace by E obtained from PCCL

RXNGF =0* AKM*EXP(-AEM/(1.987*TS1X))*ROP_s(IJK,1)*X_s(IJK,1,3)
RXNGB = ZERO

!
! h) VOLATILE MATTER --> TAR + GASES g/(cm^3.s)
! (1.0) (alphad) (1-alphad)
! (1-alphad = Sum of betad's)
!
! IF( ((X_s(IJK,1,2)/X_coal1) - VMSTAR(IJK)) .GT. ZERO) THEN
! RXNHF = C(8)*AKD*EXP(-AED*C(9)/(1.987*TS1X))*ROP_s(IJK,1)&
! * (X_s(IJK,1,2)/X_coal1)
! RXNHE = C(8)*AKD*EXP(-AED*C(9)/(1.987*TS1X))*ROP_s(IJK,1)&
! * VMSTAR(IJK)
! ELSE
! RXNHF = ZERO
! RXNHE = ZERO
! ENDIF

!
! k) CaMg(CO3)_2 ----> CaCO3 + MgO + CO2 g-mole/(cm^3.s)
!
! RXNK1F = ZERO 12.E08 * EXP(-51000./(1.987*TSORB1)) * ROP_s(IJK,1)&
! * X_s(IJK, 1, 6)/MW_s(1,6)
! RXNK1B = ZERO

!car
!car 1) CaCO3 ----> CaO + CO2 g-mole/(cm^3.s)
!car
!car

```

- Changing stoichiometric coefficients BETAD (2-6) along with for soot and C_2H_2 . CO_2 and H_2O are formed during soot oxidation hence their production equation is also added in generation equation.

```

(2) CO
  R_gp(IJK, 2) = (2. * (RXNA1F ) + RXNB1F &
    + 2. * (RXNC1F ) + RXNEB) * MW_g(2)
    + (RXNHF - RXNHB) * BETAD(2) &
    + RXNIF * BETAC(2)
  IF (X_g(IJK, 2) .GT. ZERO) THEN
    RoX_gc(IJK, 2) = (RXNB1B + 2. * (RXNC1B ) &
      + RXNEF + RXNF2F) * MW_g(2) / X_g(IJK, 2)
  ELSE
    RoX_gc(IJK, 2) = 1.0e-9
  ENDIF

(3) CO2
  R_gp(IJK, 3) = (RXNC1B + RXNEF + RXNF1F
    + F3_3 * RXNF3F &
    + RXNK1F &
    + RXNL1F &
    ) * MW_g(3) &
    + (RXNHF - RXNHB) * BETAD(3) &
    + RXNIF * BETAC(3) + RXNWF*(25.29*MW_g(3))
  IF (X_g(IJK, 3) .GT. ZERO) THEN
    RoX_gc(IJK, 3) = (RXNC1F + RXNEB + RXNL1B ) &
      * MW_g(3) / X_g(IJK, 3)
  ELSE
    RoX_gc(IJK, 3) = 1.0e-9
  ENDIF

(4) CH4
  R_gp(IJK, 4) = HALF * (RXND1F ) * MW_g(4) &
    + (RXNHF - RXNHB) * BETAD(4) &
    + RXNIF * BETAC(4)
  IF (X_g(IJK, 4) .GT. ZERO) THEN
    RoX_gc(IJK, 4) = ((RXND1B ) * HALF + RXNF1F) * MW_g(4) &
      / X_g(IJK, 4)
  ELSE
    RoX_gc(IJK, 4) = 1.0e-9
  ENDIF

(5) H2
  R_gp(IJK, 5) = (RXNB1F + RXND1B + RXNEF) &
    * MW_g(5) + (RXNHF - RXNHB) * BETAD(5) &
    + RXNIF * BETAC(5)

```

Stoichiometric coefficient of CO (0.2123)

Stoichiometric coefficient of CO_2 (0.2078) along with generation from soot oxidation reaction

Stoichiometric coefficient of CH_4 (0.0090)

Stoichiometric coefficient of H_2 (0.0515)

```

(6) H2O
  R_gp(IJK, 6) = (RXNB1B + RXNEB + 2. * RXNFOF &
    + 2. * RXNF1F + F3_6 * RXNF3F) * MW_g(6) &
    + RXNGF + (RXNHF - RXNHB) * BETAD(6) &
    + RXNIF * BETAC(6) + RXNWF*(1.538*MW_g(6))
  IF (X_g(IJK, 6) .GT. ZERO) THEN
    RoX_gc(IJK, 6) = (RXNB1F + RXNEF) * MW_g(6) &
      / X_g(IJK, 6)
  ELSE
    RoX_gc(IJK, 6) = 1.0e-9
  ENDIF

```

Stoichiometric coefficient of H_2O (0.1920) Along with generation from soot oxidation reaction

```

!      (11) C2H2
      R_gp(IJK, 11)=(RXNHF-RXNHB)* 0.0497
!      (12) SOOT
      R_gp(IJK, 12)=(RXNHF - RXNHB) * 0.2777
      IF (X_g(IJK,12).GT.ZERO) THEN
        RoX_gc(IJK,12)= RXNWF*MW_g(12)/X_g(IJK,12)
      ELSE
        RoX_gc(IJK,12)= 1.0E-09
      END IF

```

Stoichiometric
coefficient for soot (0.2777)
and C₂H₂(0.0497)

**Fate of H₂S and HCN is
not yet decided**